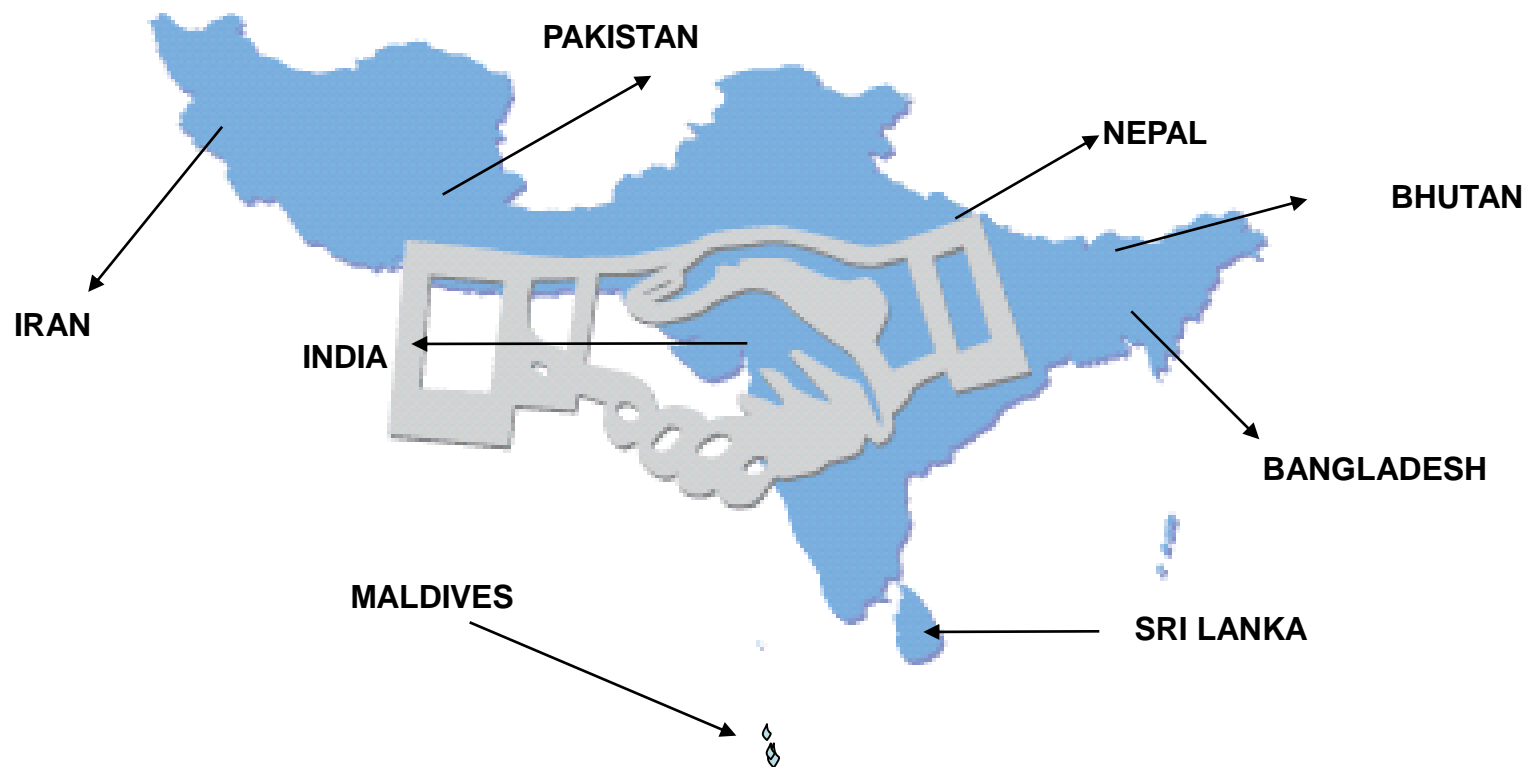# Rain water sampling and Analytical Protocol

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Mandate of Male' Declaration for Wet Deposition Monitoring

Components of Rain water Characterization

The primary parameters :
- pH, Electrical conductivity (EC)
- ionic species (SO_4^{2-}, NO_3^-, Cl-, NH_4^+, Na^+, K^+, Ca_2^+, Mg_2^+).

Notes:
- If the ion balance is out of range as per QA/QC manual, additional ions such as fluorides, bicarbonates, nitrites and organic acids may be measured
- Heavy metals, phosphate, aluminum and organic compounds may be measured for the characterization of precipitation

Wet Deposition Monitoring Protocol & Station Sitting Guidelines under Male' Declaration
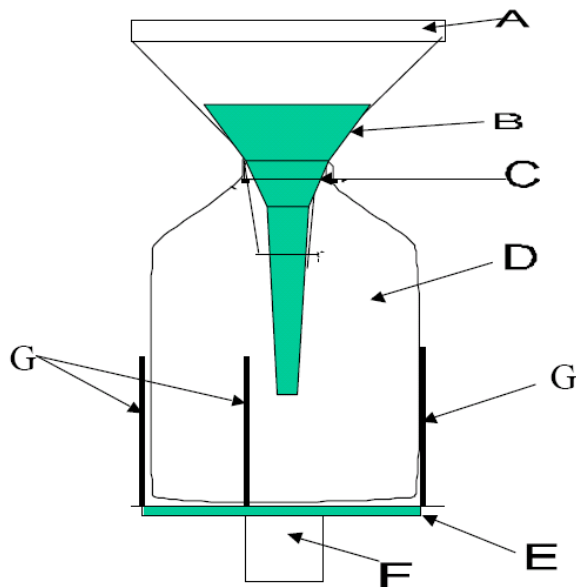
The monitoring protocol suggests the wet monitoring with

✓ **<u>Wet only collector</u>** 1 sample per week, i.e., 52 samples per year.
✓ **<u>Bulk collector</u>** 1 sample per week, i.e., 52 samples per year.

Notes:

❖   *Samples for both types should be collected for one-week periods, regardless of whether any precipitation had occurred during the previous week.*

❖   *Before collecting a new sample, the collection part of the instrument (funnel, tubing) should be cleaned thoroughly so that no contamination from the previous week remains.*

Figure 1: Open field collector for percipitation. **A:** *Funnel of polyetene ca 200 mm dia.* **B:** *Inner funnel of polyetene with small opening.* **C:** *Cap, leakage free connection.* **D:** *Polyetene bottle (5L).* **E:** *Bottom plate fastened onto the pole.* **F:** *Pole of wood (50x50 mm) length ca 110 cm above ground.* **G:** *Four rods to keep the equipment in place.*

Figure 1: Bulk Collector

Figure 2: Wet only Collector   **Figure 2a: Funnel & Bottle**   **Figure 2b: Solar Panel**

Sampling Devices

Bulk Collector
It consists of a funnel (0.5-1 m dia) connected to a 5 or a 10 L collection bottle (size depending on rainfall) by a pipe. All materials should be wrapped with aluminium. The funnel should hold at a height of 1-1.5 m from ground level with the help of a stand. The funnel should be protected from bird droppings, etc.

Wet only collector:
An automatic wet only collector consists of a collecting bucket or funnel, a lid that can be opened and closed, a precipitation sensor, and a sample container.

A wet and dry collector is also acceptable to collect precipitation samples. Versions, which are composed of two collection buckets. one for collection of precipitation during the wet period and the other for collection of dry fallout during the dry period.

Guidelines for Sampling Instrument placement and installation

The criteria for the placement of monitoring instruments at a remote deposition monitoring site are:

- An open, flat area free from any obstructions.

- No objects should be within a few meters which can 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 30⁰ 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.

Cautions in case of Stationing both Dry and Wet Deposition Sampling Devices at same location

➤ The horizontal distance between wet and dry collector and rain gauge if provided, Dry Deposition collector should be greater than 2 meters.

➤ One of the bulk samplers should be placed proximate 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.

➤ Wet only collectors and bulk collectors require no special protection during rains.

➤ The control box and battery of the wet only collector should be placed in a shaded area, away from rain.

Analytical Methods

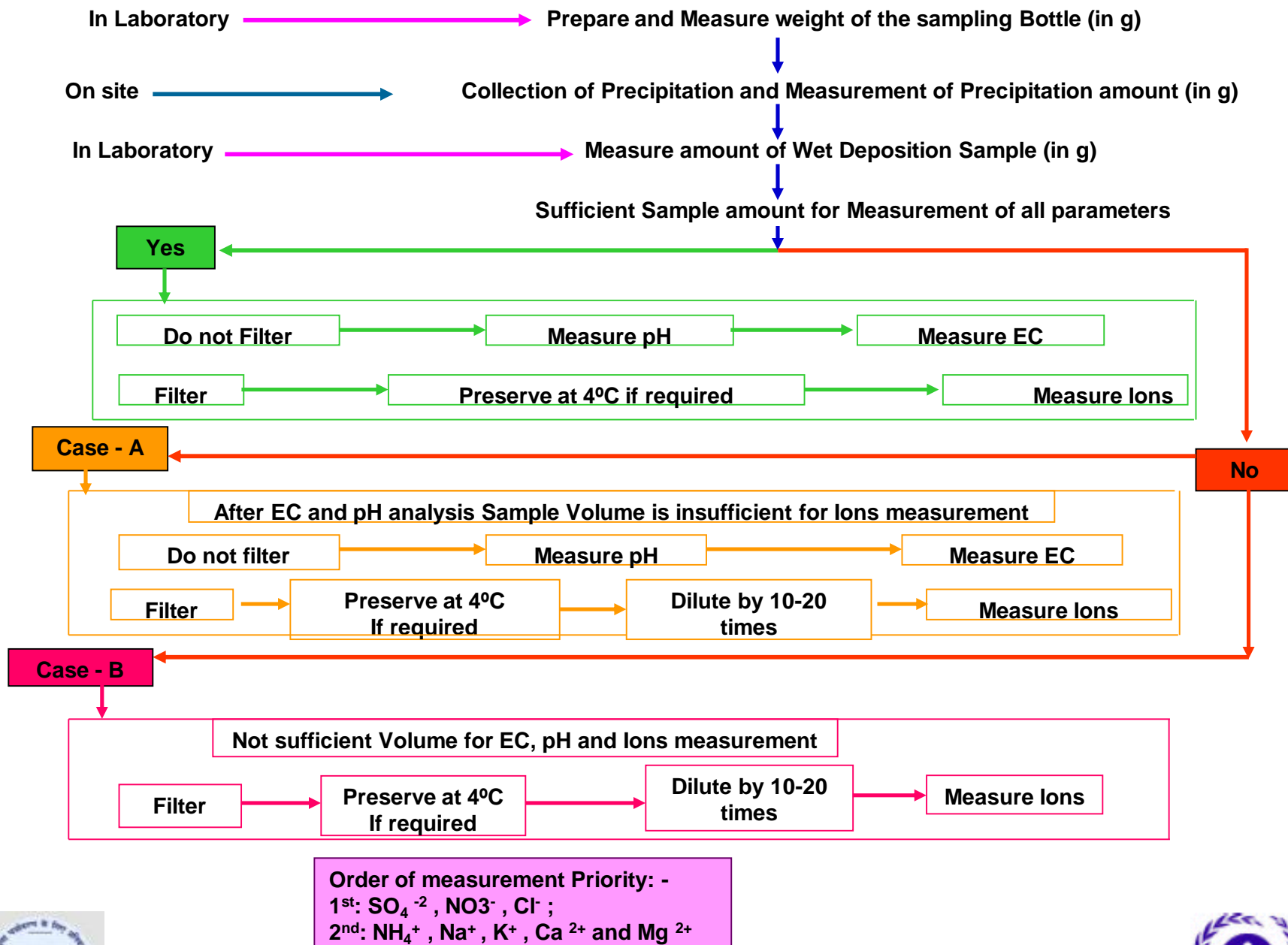## Table 1 Procedures Suggested for Rainwater Major Constituent Analysis

Parameter	Instrument method
Electric Conductivity	Conductivity Cell
pH	Glass electrode (preferably with the Electrode of non-leak inner cell)
Chloride	Argentrometric method
Nitrate	Cadmium reduction method Spectrophotometry
Sulphate	Spectrophotometry
Ammonium	Spectrophotometry (Indophenol method)*
Sodium	Flame photometry
Potassium	Flame photometry
Calcium	Titrimetry (EDTA method)
Magnesium	Titrimetry

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

** Thymol (2-isopropyl-5-methyl phenol)

Ion analysis using Ion-Chromatograph may a better option if the samples are properly transported to Laboratory

In Laboratory → **Prepare and Measure weight of the sampling Bottle (in g)**

↓

On site → **Collection of Precipitation and Measurement of Precipitation amount (in g)**

↓

In Laboratory → **Measure amount of Wet Deposition Sample (in g)**

↓

Sufficient Sample amount for Measurement of all parameters

↓

Yes

Do not Filter →	**Measure pH** →	**Measure EC**
Filter →	**Preserve at 4ºC if required** →	**Measure Ions**

Case - A ← **No**

After EC and pH analysis Sample Volume is insufficient for Ions measurement

Do not filter →	**Measure pH** →	**Measure EC**
Filter →	**Preserve at 4ºC If required** →	**Dilute by 10-20 times** →	**Measure Ions**

Case - B

Not sufficient Volume for EC, pH and Ions measurement

Filter →	**Preserve at 4ºC If required** →	**Dilute by 10-20 times** →	**Measure Ions**

Order of measurement Priority: -
1st: SO_4^{-2} , $NO3^-$, Cl^- ;
2nd: NH_4^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+}

Wet Deposition Sample Flow chart

Analytical Work Instruction (Brief SOPs)

pH – (Apparatus – pH meter, Glass Electrode, Reference Electrode)

- ➤ Switch on pH meter, allow it to warm up and stabilise
- ➤ Take pH 4.0 Buffer solution and immerse the electrodes in it
- ➤ Press 'CAL' to calibrate the instrument at pH 4.0
- ➤ Immerse the electrodes in pH buffer 9.0, press 'CAL' to calibrate at pH 9.0
- ➤ To check the calibration immerse the electrodes in pH 7.0 buffer. If the reading agrees within ± 0.05, the system is ready to proceed for sample analysis
- ➤ Indicate the Temperature of sample with pH value

Electrical Conductivity – (Apparatus – Conductivity meter, Conductivity Cell Thermometer)

- ➤ Switch on Conductivity meter, allow it to warm up and stabilise
- ➤ Calibrate the instrument with 0.01 (N) Standard Potassium Chloride solution which has a conductivity of 1412 µ mhos /cm at 25ºC.
- ➤ Measure the conductivity of sample at 25 ºC

THESE TWO PARAMETERS SHOULD ALWAYS BE DONE WITHOUT FILTRATION AND ANY DILUTION

Analytical Work Instruction (Brief SOPs)

CHLORIDE – Argentometric Titration
(Reagents – 0.0141 (N) Silver Nitrate, 0.0141 (N) Standard Sodium Chloride and Potassium Chromate Indicator)
  ➢ **Take 100 ml sample or an aliquot diluted to 100 ml**
  ➢ **Add 1ml Potassium Chromate Indicator**
  ➢ **Titrate with Silver Nitrate Solution standardized against Standard NaCl solution**
  ➢ **Calculate the Cl⁻ value using following formula**

pH adjustment may be required if pH of sample is below 7.0 or above 10

$$\text{Chlorides as Cl}^- \text{ mg/L} = \frac{(V_1 - V_2) \times N \times 35.45 \times 1000}{\text{ml Sample}}$$

Where,

V_1	=	Volume of silver nitrate required for sample, in ml
V_2	=	Volume of silver nitrate required for reagent blank, in ml
N	=	Normality of Silver Nitrate.

Analytical Work Instruction (Brief SOPs)

SULPHATE – Spectrophotometric method
Reagents – (Conditioning reagent, Barium Chloride crystals, Standard Sulphate solution 1ml = 0.1 mg)
Apparatus – Spectrophotometer, Magnetic stirrer, Stopwatch

- Take 10, 20, 30, 40 and 50 ml of standard sulphate solution in 250 ml flask
- make the volume up to 100 ml
- Add 5 ml Conditioning reagent, stir on magnetic stirrer one by one
- While stirring add a scoop of Barium chloride (0.5 g)
- After 30 seconds immediately take a portion in absorption cell and record the absorbance at 420 nm every 30 seconds up to 4 minutes.
- Repeat the same for all standards
- Plot a calibration curve
- Take 100 ml sample, proceed as calibration steps
- Calculate the SO_4^{2-} value from Calibration curve

Analytical Work Instruction (Brief SOPs)

Total Hardness – EDTA Titrimetric method
Reagents – (Buffer Soln, Standard EDTA 0.01(M) soln., 0.1(M) Standard Calcium soln., EBT.)

Apparatus – Spectrophotometer

- **Take 100 ml sample or an aliquot diluted to 100 ml**
- **Add 2 ml Buffer soln.**
- **Pour 0.2 - 0.4 g EBT**
- **Titrate with EDTA Solution standarised against Standard Calcium solution**
- **Calculate the Total Hardness value using following formula**

$$\text{Hardness as mg/l } CaCO_3 = \frac{(V_1 - V_2) \times A \times 1000}{\text{ml sample}}$$

Where

V_1 is the volume of EDTA required for sample

V_2 is the volume of EDTA required for reagent blank

A is the mg $CaCO_3$ equivalent to 1.00 ml EDTA titrant

Analytical Work Instruction (Brief SOPs)

Calcium and magnesium – EDTA Titrimetric method Reagents – (NaOH Buffer Soln, Standard EDTA 0.01(M) soln., 0.1(M) Standard Calcium soln., Murexide.)

Apparatus – Spectrophotometer

- ➤ **Take 100 ml sample or an aliquot diluted to 100 ml**
- ➤ **Add 5 ml NaOH soln.**
- ➤ **Pour 0.2 - 0.4 g Murexide**
- ➤ **Titrate with EDTA Solution standarised against Standard Calcium solution**
- ➤ **Calculate the Total Hardness value using following formula**

Calcium hardness as mg CaCO/l $= \dfrac{(V_1 - V_2) \times A \times 1000}{\text{ml sample}}$

Where,

V_1 is the volume of EDTA required for sample.
V_2 is the volume of EDTA required for reagent blank.
A is the mg $CaCO_3$ equivalent to 1.00 ml EDTA titrant.

Calcium as Ca^{++} (mg/l) = Calcium hardness as $CaCO_3$ mg/l $\times$ 0.4

Magnesium as equivalent $CaCO_3$ may easily be estimated as the difference between total hardness and calcium hardness as $CaCO_3$:

Magnesium as Mg^{++} mg/l =

(Total Hardness as mg $CaCO_3$/l - Calcium Hardness as mg $CaCO_3$/l) $\times$ 0.243

Analytical Work Instruction (Brief SOPs)

Sodium and Potassium – Flame Photometric Method
Reagents – (Na & Potassium Standard soln. in different ranges, 0 – 1.0 ppm, 1.0 – 10 ppm and 10 – 100 ppm)

Apparatus – Flame Photometer

> **Prepare calibration curve at desired range / ranges**
> **analyse sample (direct or after dilution)**
> **Calculate the Na / K values using Calibration graph**

Analytical Work Instruction (Brief SOPs)

Ammonium ion – Indophenol blue Method (Spectrophotometric)
Reagents – (Phenol soln., Sodium nitroprusside (0.5% v/v) soln., oxidizing agent (Alkaline citrate + Sodium hypochlorite) Standard Ammonia solution

Apparatus – Flame Photometer

- **Take 25 ml sample in flask**
- **Add 1.0 ml phenol solution**
- **Add 1.0 ml Nitroprusside soln.**
- **Add 2.5 ml Oxidising reagent**
- **Cover and allow it to react at 22 – 27 ºC for at least an hour in subdued light**
- **Take absorbance at 630 nm**
- **Prepare and process the standards in same way**
- **Prepare calibration curve**
- **Calculate sample concentration from Calibration graph**

Analytical Work Instruction (Brief SOPs)

Nitrite and Nitrate – Spectrophotometric
Reagents and Reduction coulmn– (Sulphanylamide, NEDA, Standard Nitrite and Nitrate soln. Ammonium Chloride Buffer, Cadmium Column)

Apparatus – Spectrophotometer

Nitrite
- **Take 50 ml sample in nessler's tube**
- **Add 1.0 ml Sulphanylamide.**
- **Add 1.0 ml NEDA soln.**
- **Wait for colour development**
- **Take absorbance at 543 nm**
- **Prepare and process the standards in same way**
- **Prepare calibration curve**
- **Calculate sample concentration from Calibration graph**

For Nitrite + Nitrate reduce the sample through Cadmium reduction column
Follow the same steps for colour development and analysis

To report only Nitrate Subtract the nitrite value from Nitrate + Nitrite

Minimum required Sample Volume for rain water Analysis

Parameters	Suggested Methods	Sample Volume required as per Method	Minimum required sample volume	If 10 – 20 times dilution is considered for ions the minimum Sample
pH	By pH Meter	50 ml	20-25 ml	20-25 ml
Conductivity	Conductivity Cell	50 ml	20-25 ml	20-25 ml
Sulphate (SO_4^{2-})	Spectrophotometric	100 ml	50 ml	2.5 – 5.0 ml
Chloride (Cl^-)	Argentometric	100 ml	50 ml	2.5 – 5.0 ml
Nitrate (NO_3^-)	Cadmium reduction & spectrophotometric	50 ml (for reduction) + 25 ml for NO_2^-	50 ml	2.5 – 5.0 ml
Ammonium (NH_4^+)	Spectrophotometric	50 ml	25ml	1.25 – 2.5 ml
Sodium (Na^+)	Flame Photometry	50 ml	20ml	1.0 – 2.0 ml
Potassium (K^+)	Flame Photometry			
Calcium (Ca^{2+})	EDTA Titration	200 ml (100 ml for T.H. + 100 ml for Calcium Hardness	50 ml	2.5 – 5.0 ml
Magnesium (Mg^{2+})	By Calculation	Nil	Nil	Nil
Total		**675 ml**	**285 – 295 ml**	**52.25 – 74.5**

If Ions are analysed by Ion Chromatography the required sample volume reduces drastically				
pH	Conductivity	Three Anions	Five Cations	Total
20 – 25 ml	20 – 25 ml	10 ml	10 ml	60 – 70 ml

Advantages – More accurate and precise, 8 parameters required only 2 runs
Disadvantages – More capital investment

Wet deposition samples: For wet deposition samples the detection and determination limits are:

(both :determined as specified in Appendix 4; unit μmol/L)

Parameter	Detection limit	Determination limit
SO_4^{2-}	0.3	1.0
NO_3^-	0.5	1.5
Cl^-	0.5	1.5
NH_4^+	0.8	3.0
Na^+	0.3	1.0
K^+	0.3	1.0
Ca^{2+}	0.2	0.6
Mg^{2+}	0.3	1.0

pH Replicate measurement of RM* should agree to within ±0.05 pH value of RM

EC Replicate measurement of deionized water (EC: less than 0.15mS/m) should agree to within ±0.02mS/m

* - RM: Reference material

Thank You

About Ion Chromatography

Chromatography (from Greek *chroma*, color and *graphein* to write) is the collective term for a family of laboratory techniques for the separation of mixtures. It involves passing a mixture dissolved in a "mobile phase" through a *stationary phase*, which separates the analyte to be measured from other molecules in the mixture and allows it to be isolated.

Ion exchange chromatography retains analyte molecules based on coulombic (ionic) interactions. The stationary phase surface displays ionic functional groups (R-X) that interact with analyte ions of opposite charge.

➤   **Cation exchange chromatography**
➤   **Anion exchange chromatography.**

Cation exchange chromatography retains positively charged cations because the stationary phase displays a negatively charged functional group

$$R\text{-}X^-C^+ + M^+B^- \rightleftarrows R\text{-}X^-M^+ + C^+ + B^-$$
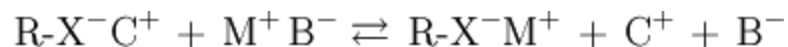
Anion exchange chromatography retains anions using positively charged functional group

$$R\text{-}X^+A^- + M^+B^- \rightleftarrows R\text{-}X^+B^- + M^+ + A^-$$
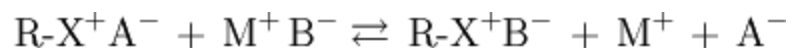
Note that the ion strength of either C+ or A- in the mobile phase can be adjusted to shift the equilibrium position and thus retention time.

Typical Ion Chromatogram
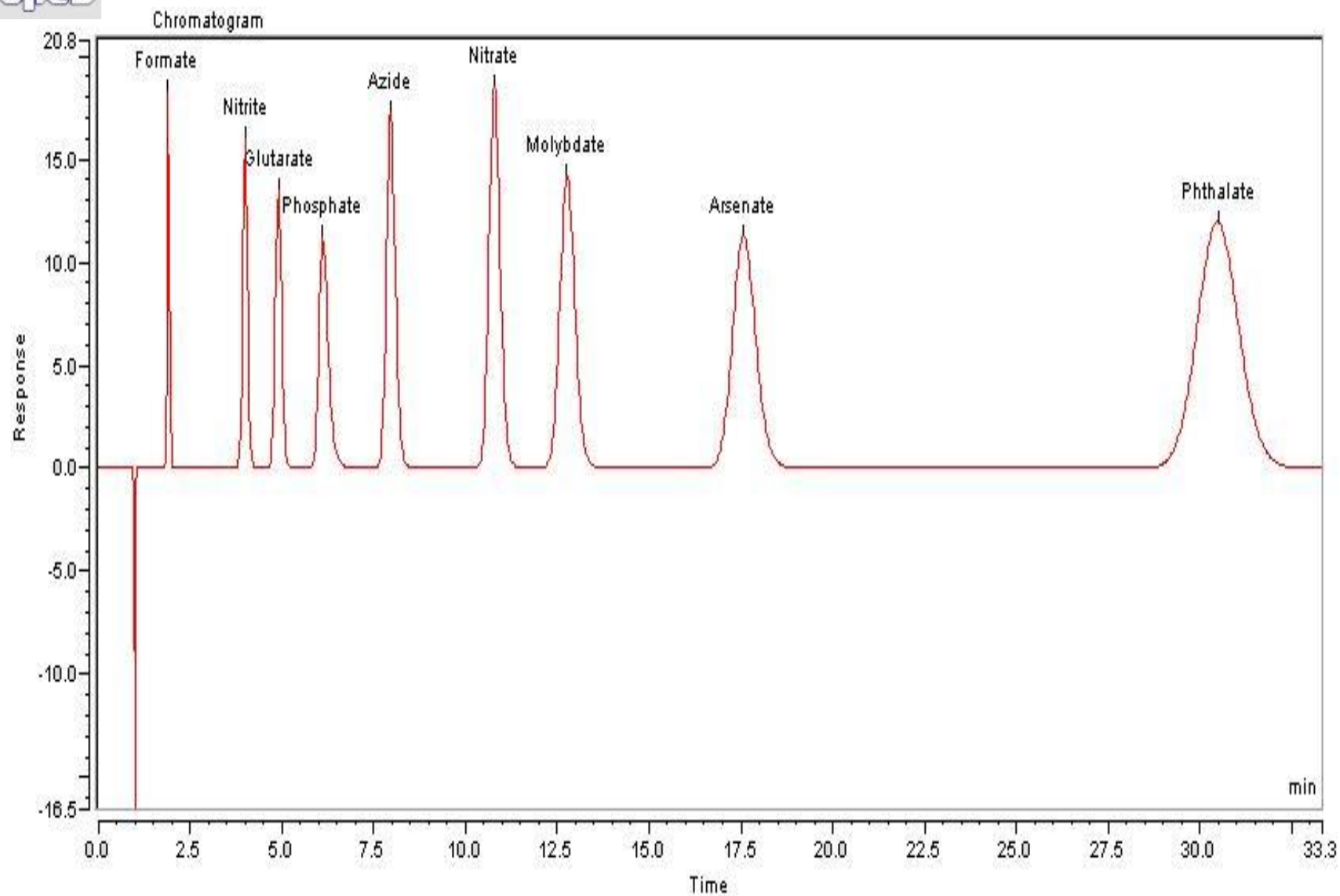
WATER

H₂SO₄

suppressor

Conductivity
Detector

Eluent & Injected
Sample Waste

Anion Route

1

2

3

A

833 Liquid Handling
Unit

A Supp 5 Anion Column

Injector

Water waste

H₂SO₄   Waste

Valve

818 IC
pump

Pulse
Dampener

Anion E
luent
Bottle

E luent
Waste

WATER

H₂SO₄

suppressor

Conductivity
Detector

Eluent & Injected
Sample Waste

Cation Route

1

2

3

A

**833 Liquid Handling
Unit**

A Supp 5 Anion Column

Injector

Water waste

H₂SO₄   Waste

Valve

818 IC
pump

Anion
E luent
Bottle

Pulse
Dampener

E luent
Waste

cpcb

UNEP

Ion chromatograph

Technical information

Carrier material	polyvinyl alcohol with quaternary ammonium groups
Column dimensions	4.0 x 250 mm
Column body	PEEK
Standard flow	0.7 mL/min
Maximum flow	0.8 mL/min
Maximum pressure	15 MPa
Particle size	5 μm
Organic modifier	0 ...100%
pH range	3...12
Capacity	94 μmol (Cl⁻)

Eluent

Carbonate eluent (standard eluent)

| Sodium hydrogen carbonate | 168 mg/2 L | 1.0 mmol/L |
| Sodium carbonate | 678 mg/2 L | 3.2 mmol/L |

Metrosep A Supp 5 – 250 (6.1006.530)

Technical information

Carrier material	silica gel with carboxyl groups
Column dimensions	4.0 x 250 mm
Column body	PEEK
Standard flow	1.0 mL/min
Maximum flow	5 mL/min
Maximum pressure	35 MPa
Particle size	7 μm
Organic modifier	0 ...100% (no methanol)
pH range	2...7
Capacity	194 μmol (K⁺)

Eluents

Tartaric acid-dipicolinic acid eluent (standard eluent)

| Tartaric acid | 1200 mg/2 L | 4.0 mmol/L |
| Dipicolinic acid | 250 mg/2 L | 0.75 mmol/L |

Nitric acid eluent

| Nitric acid (c = 1 mol/L) | 4 mL/2 L | 2.0 mmol/L |

Metrosep C 2 – 250 (6.1010.230)

Cations	Salt	Weights in (g)	Final Volume	Concentrations
Sodium	NaNO3	3,6971	1000 mL	1000 mg/L
Ammonium	NH4Cl	2,9654	1000 mL	1000 mg/L
Potassium	KNO3	2,5858	1000 mL	1000 mg/L
Calcium	Ca (NO₃)₂ ,4H₂O	5,8920	1000 mL	1000 mg/L
Magnesium	Mg(NO₃)₂ × 6 H₂O	10,5467	1000 mL	1000 mg/L

Prepare Standard Mix - A Solution containing 100 ppm each Na+ and NH4+ from 1000-ppm stock by diluting the same.

**Prepared Standard Mix – B** solution containing 100 ppm each K+, Ca++ and Mg++ by diluting the stock. Final calibration standards for 5 levels are prepared following the Table VIII (b) given below. Prepare fresh working calibration standards weekly and refrigerate when not in use. Stock Standards may be used for 6 months if refrigerated properly.

Ions	Level I 0.50 ml A + 1.0 mL B	Level II 1 ml A + 2 mL B	Level III 2 ml A + 4 mL B	Level IV 4 ml A + 8 mL B	Level V 5 ml A + 10 mL B
Sodium	0.50	1.0	2.0	4.0	5.0
Ammonium	0.5	1.0	2.0	4.0	5.0
Potassium	1.0	2.0	4.0	8.0	10.0
Calcium	1.0	2.0	4.0	8.0	10.0
Magnesium	1.0	2.0	4.0	8.0	10.0

Eluent for Cations: Specific for brand and make to instrument and columns being used. Generally for cation analysis Weigh 600 mg of **Tartaric Acid** and 167 mg Dipicolinic **Acid** and dissolve in 100 ml of ultra pure water (HPLC/Milli-Q Grade). Make up the volume to 1 Liter with Milli-Q Water. Eluents are required to be filtered through 0.22 µm nylon filter.

Anions	Salt	Weights in (g)	Final Volume	Concentrations
Fluoride	NaF	2.2100	1000 mL	1000 mg/L
Chloride	NaCl	1.6484	1000 mL	1000 mg/L
Bromide	NaBr	1.4998	1000 mL	1000 mg/L
Nitrite	NaNO₂	1.2877	1000 mL	1000 mg/L
Nitrate	NaNO₃	1.4330	1000 mL	1000 mg/L
Phosphate	KH₂PO₄	1.3707	1000 mL	1000 mg/L
Sulphate	Na2SO4	1.4790	1000 mL	1000 mg/L

Prepare Standard Mix - C Solution containing 100 ppm each Cl-, NO3- and SO4= from 1000 ppm stock by diluting the same.

**Prepared Standard Mix – D** solution containing F- (5 ppm) and Br-, NO2 -, PO4-3, 20 ppm each by diluting the stock. Final calibration standards for 6 levels are prepared following the Table VIII (d) given below. Prepare fresh working calibration standards weekly and refrigerate when not in use. Stock Standards may be used for 6 months if refrigerated properly.

Ions	Level I	Level II	Level III	Level IV	Level V	Level VI
	0.5 C + 0.5 D	1 C + 1 D	2 C + 2 D	5 C + 5 D	10 C + 10 D	15 C + 1 5 D
Fluoride	0.025	0.05	0.1	0.25	0.5	1.0
Chloride	0.5	1.0	2.0	5.0	10.0	15.0
Bromide	0.1	0.2	0.4	1.0	2.0	3.0
Nitrite	0.1	0.2	0.4	1.0	2.0	3.0
Nitrate	0.5	1.0	2.0	5.0	10.0	15.0
Phosphate	0.1	0.2	0.4	1.0	2.0	3.0
Sulphate	0.5	1.0	2.0	5.0	10.0	15.0

Note: All the aliquot volume is in ml

Eluent for Anions: Specific for brand and make to instrument and columns being used. For concentration and composition of eluent please refer to the application notes. Generally for anion analysis NaHCO3 - Na2CO3 eluent is used. Eluents are prepared by dissolving prescribed amount of chemicals in high purity nano-pure distilled water. Eluents are required to be filtered through 0.22 µm nylon filter.

Calibration of Anions
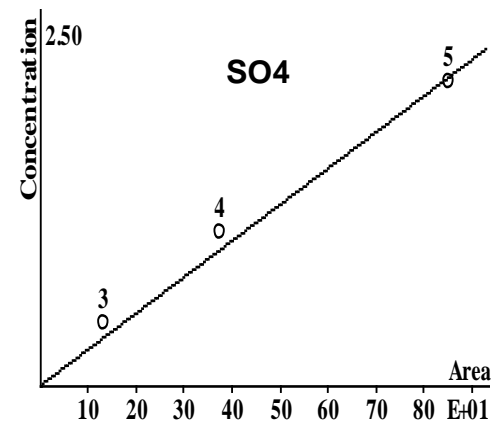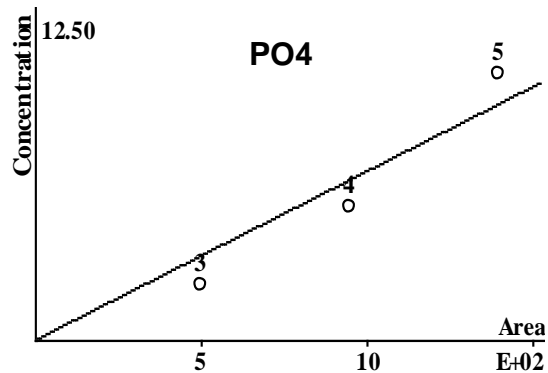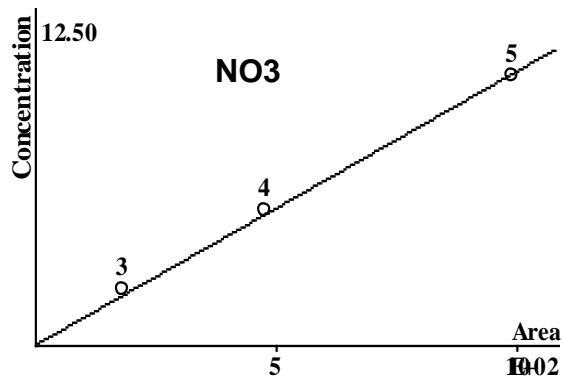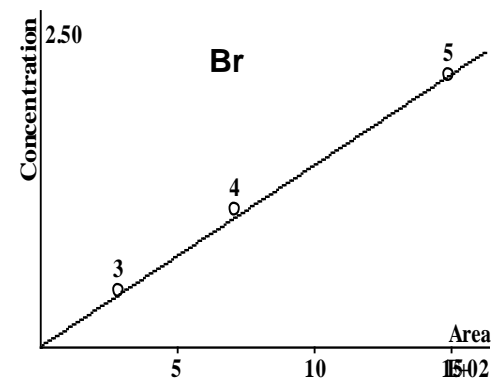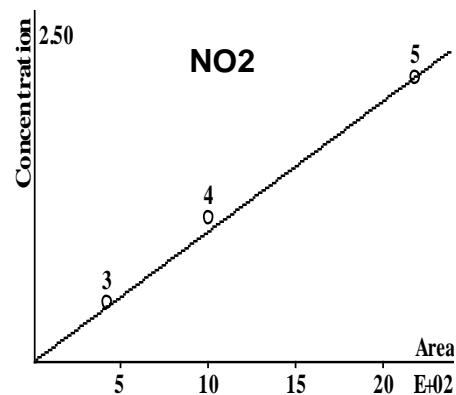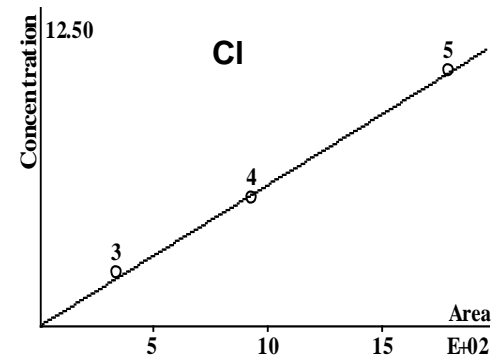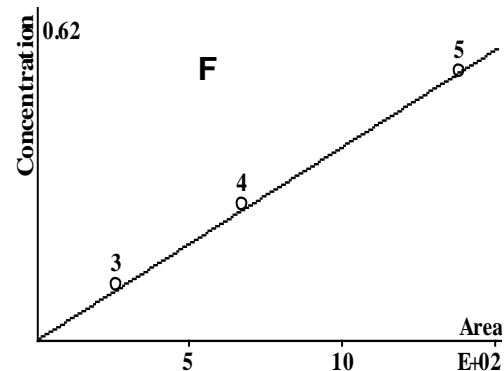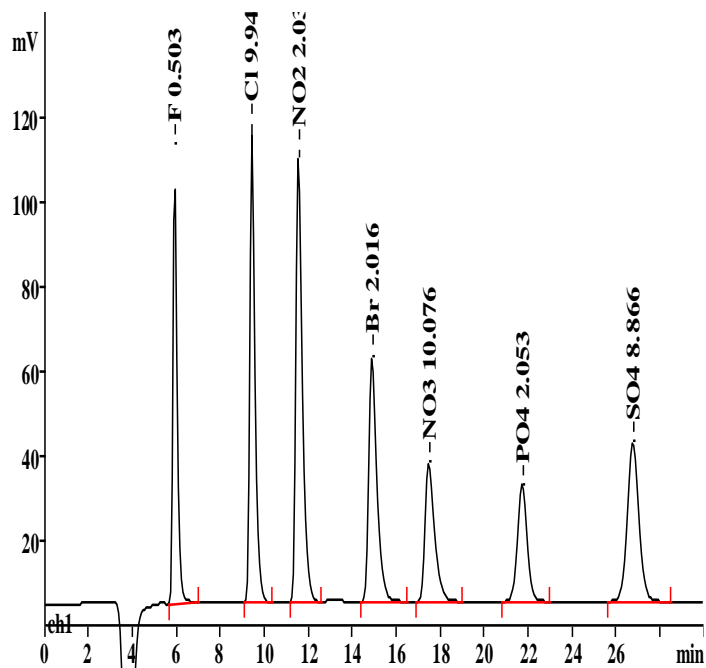
Analytical precision (Si) is computed for wet deposition and the AAQ gaseous samples and is calculated with following formula:

$$S_i = \frac{(Sd_i^2/2N_i)^{1/2} \times 100}{Av}$$

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

Sample #	Result 1 (mg/L)	Result 2 (mg/L)	Difference d (mg/L)	Average Av (mg/L)
1.	50	46	4	48.0
2.	37	36	1	36.5
3.	22	19	3	20.5
4.	17	20	3	18.5
5.	32	34	2	33.0

$Sd_i^2 = 4^2+1^2+3^2+3^2+2^2 = 39$
$N_i = 5$
$Av = \dfrac{48+36.5+20.5+18.5+33}{5} = 31.5$
$S_i = 6.27\%$, which meets the DQO