The Abdus Salam International Centre for Theoretical Physics

The International Union of Geodesy and Geophysics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

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**Workshop on Atmospheric Deposition: Processesand Environmental Impacts**

***21 - 25 May 2012***

# Deposition Measurements: Sampling and Analysis

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# Deposition Measurements: Sampling and Analysis

ICTP 22 may 2012

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Laboratoire d'Aérologie

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# Summary

Deposition sampling:

- Constraints
- Dry deposition
- Wet deposition

Sample analysis:

- Overwiew of techniques used
- Quality Assurance/ Quality control

# Sampling constraints on sites: local positionning

Naturally vegetated, level area is preferred

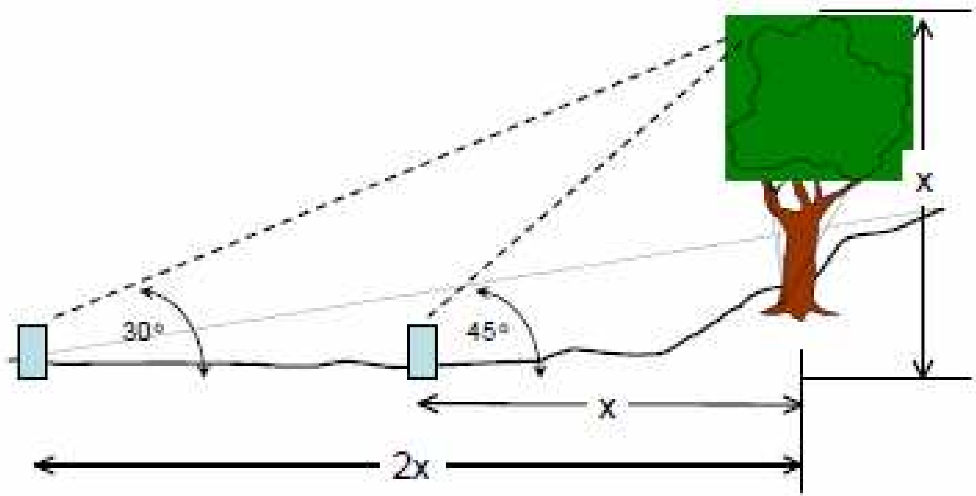
Maintain the height of vegetation less than 0.5 meters

Ground cover should surround the samplers for a distance of 30 meters

Structures projection angles:

30 degrees optimal, 45 degrees maximum

30 metres minimum away of dwellings



# Sampling constraints on sites global positionning

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

| Potential Interference | Minimum Distance to Site (km) Global | Regional | Examples, Notes and Local Considerations |
|---|---|---|---|
| $SO_2$ or $NO_x$ Point Source | | | If emission sources (such as power plants, refineries, |
| >100 tonnes per year | 50 | 20 | chemical plants, smelters or other major industrial facilities) |
| >1000 tonnes per year | 100 | 50 | are located in the general upwind direction from the collector, |
| Major Industrial Complex | 150 | 50 | then the regional distances indicated should be doubled. |
| Town, population 1,000-10,000 | 25 | 10 | Future population growth and associated land development |
| Town, population 10,000-25,000 | 50 | 20 | should be considered carefully, especially for towns and |
| City, population 25,000-100,000 | 100 | 50 | villages near a station. If population centres are located in |
| City, population >100,000 | 200 | 100 | the general upwind direction from the collector, then the regional distances indicated should be doubled. |
| Major highway, airport, railway, shipping lane, harbour | 25 | 5 | Moving sources of pollution, such as air, ground, or water traffic or the medium on which they traverse (e.g., runway, taxiway, road, tracks, or navigable river), should not be within 500 metres of the collector. |
| Secondary road, heavily travelled | 5 | 1 | The local road network around the site is of particular |
| Secondary road, lightly travelled | 1 | 0.5 | concern. Traffic volume and type as well as road surface will largely determine the impact at the site. |
| Feedlot operations | 50 | 2 | Acceptable distances will vary greatly depending on size of the operation. Even small concentrations of animals should be housed no closer than 500 metres. If the feedlot, dairy barn or animal waste pile can be smelled at the collector, it is too close. |
| Intensive agricultural activities | 10 | 2 | Surface storage of agricultural products, fuels, vehicles or other source materials should be kept at least 500 metres from the collector. |
| Limited agricultural activities | 1 | 0.4 | Storage of small amounts of agricultural products, fuels, or other source materials should be kept at least 200 metres from the collector and well sealed. |
| Parking lot or large paved area | 0.5 | 0.2 | On-site parking lots and maintenance yards also need to be kept at least 300 metres from the collector. |
| Building with fuel combustion | 1 | 0.4 | |
| Sewage treatment plant | 20 | 2 | |
| Active volcano, fumarole, etc. | 100 | 20 | Geothermal sites including geysers and springs may have significant emissions and should be avoided. |
| Natural salt, dust, alkali sources | 2 | 2 | Windswept materials from salt and alkali flats as well as sea spray from coastlines can contaminate samples. |
| Tree line, building | 0.05 | 0.05 | |

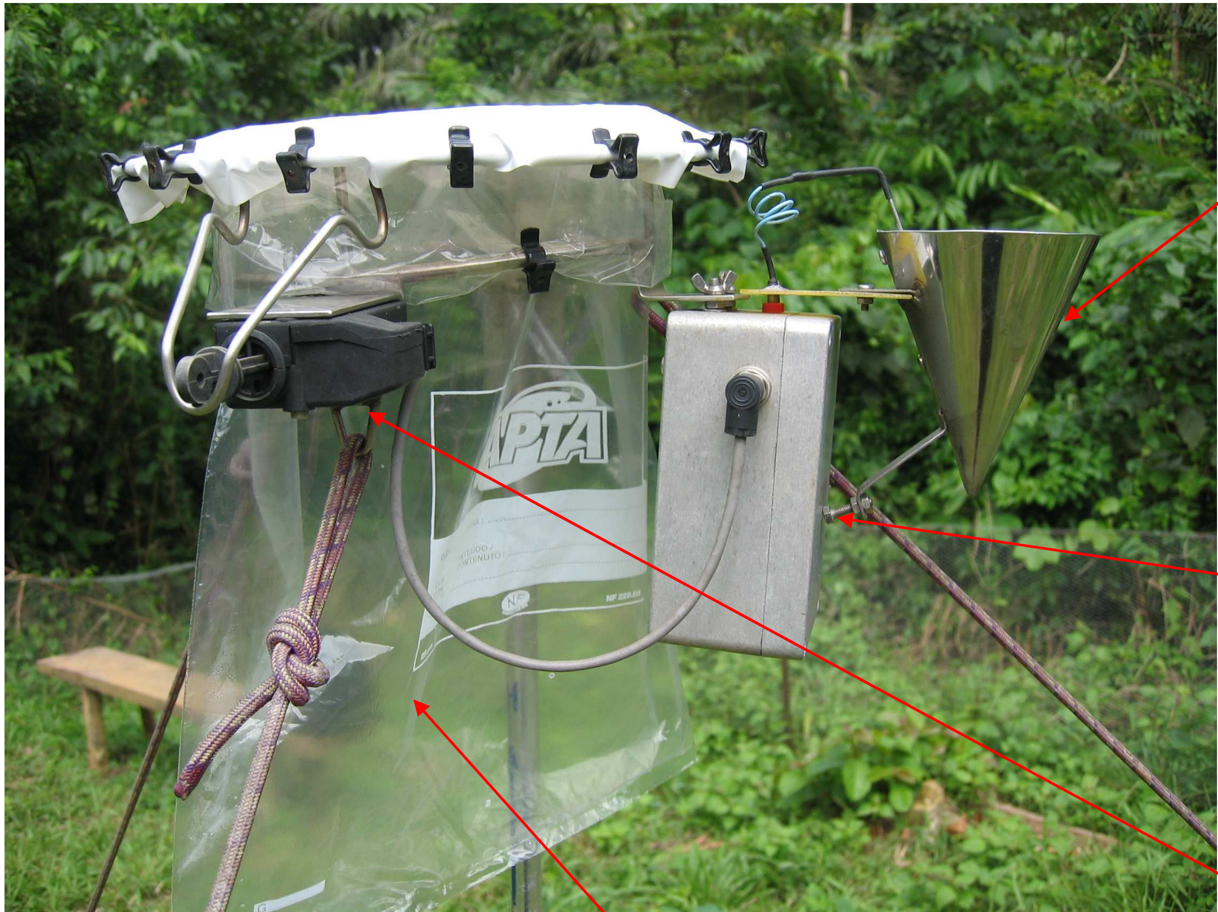
# IDAF station : DJOUGOU (BENIN)

Passive samplers

Rain sampler

Aerosols sampler

# Wet depostion: IDAF rain collector




Rain detector

Power supply

Automatic opening system

Single-use plastic bag

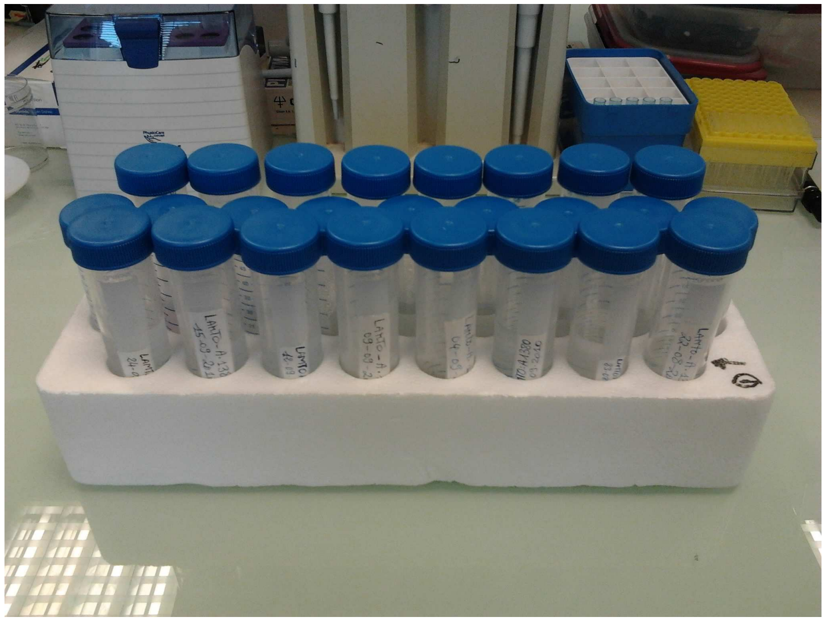
# Wet deposition

Rain samples storage: GREINER centrifugation tubes (50 mL) filled and labelled after each rainy event

Rain samples preservation:

Best: freezing in site to -18℃ and kept frozen until an alysis

Alternative: adding thymol or formol to avoid bacterial activity



# Dry deposition: gases by passive samplers

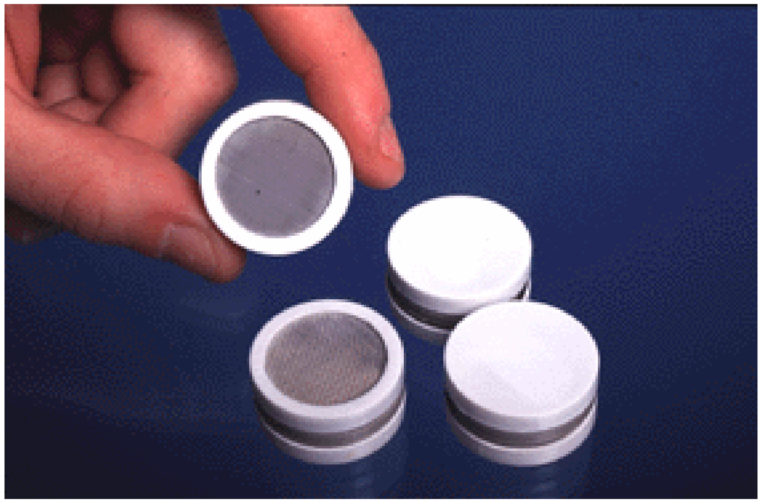
IDAF Passive samplers holders:
8 samplers exposed together

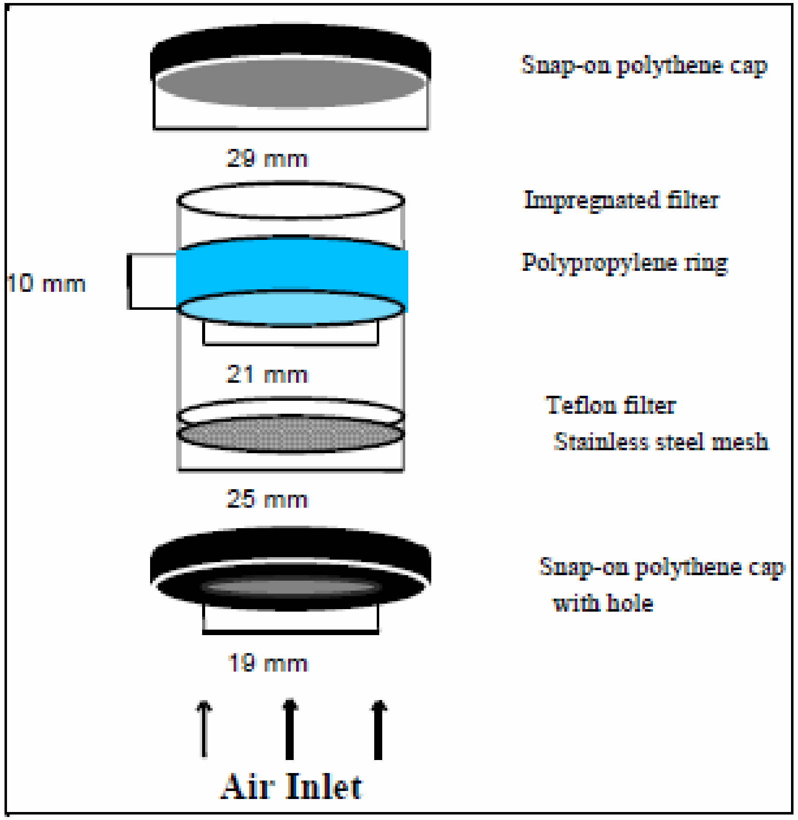
# Dry deposition: gazes by passive samplers

IDAF sampler: developped in the Laboratoire d'Aérologie

Based on M. Ferm work

(IVL 1991, 1994)





# Passive samplers

2 weeks or one month exposure, the impregnated paper filters react with gazes present in ambiant air and form species which can be measured in water by ion chromatography

IDAF samplers are colored to be easily identified ,they are exposed by duplicates to ensure precision and reproducibility

Shipped to the IDAF stations by mail; stored in fridge (4℃ before and after exposure)

| Gas (Colour of the sampler) | Coating solution | Chemical reaction on the filter |
|---|---|---|
| $HNO_3$ and $SO_2$ (Black) | 0.5 g NaOH in 50 mL methanol (pH>12) | $HNO_3(g)\ OH^- \rightarrow NO_3^- + H_2O$<br>$2SO_2(g)+4OH^-+O_2 \rightarrow 2H_2O+2SO_4^{-2}$ |
| $NO_2$ (Grey) | 0.44 g NaOH + 3.95 g NaI in 50 mL methanol (pH>12) | $2NO_2(g)+3I^- \rightarrow 2NO_2^- + I_3^-$ |
| $NH_3$ (White) | 1.0 g citric acid in 50 mL methanol | $NH_3(g)+H^+ \rightarrow NH_4^+$ |
| $O_3$ (Grey & black) | 0.25 g $NaNO_2$ + 0.25 g $K_2CO_3$ + 0.5 ml redistilled glycerol in 50 ml water | $O_3(g)+NO_2^- \rightarrow NO_3^- + O_2$ |

# Passive samplers

Calculation of gases concentration: Fick's first law of diffusion

$$C_{avg}(ppb) = [(L/A).X.R.T] / (t.D.P)$$

L/A : depends of the sampler's physical caracteristics ($m^{-1}$)

X : amount of gas pollutant trappped on the filter ($\mu$mol)

R : ideal gaz constant (atm $K^{-1}$ $mol^{-1}$)

t : exposure time (s)

P : mean atmospheric pressure during exposure (atm)

T : mean temperature during exposure (K)

D : diffusion coefficient of the wanted gas in air ( $m^2$ $s^{-1}$)

# Passive samplers

Easy to use, no electricity supply needed

Good reproducibility (10-20 %)

Mean gas concentrations values during the exposition period

Good agreement active/passive measurements for $NO_2$, $SO_2$ and $O_3$

# Dry Deposition: gazes

# measurements by Relaxed Eddy Accumulation (REA)

Air mass selection according to the sign of the vertical speed (+ or -)

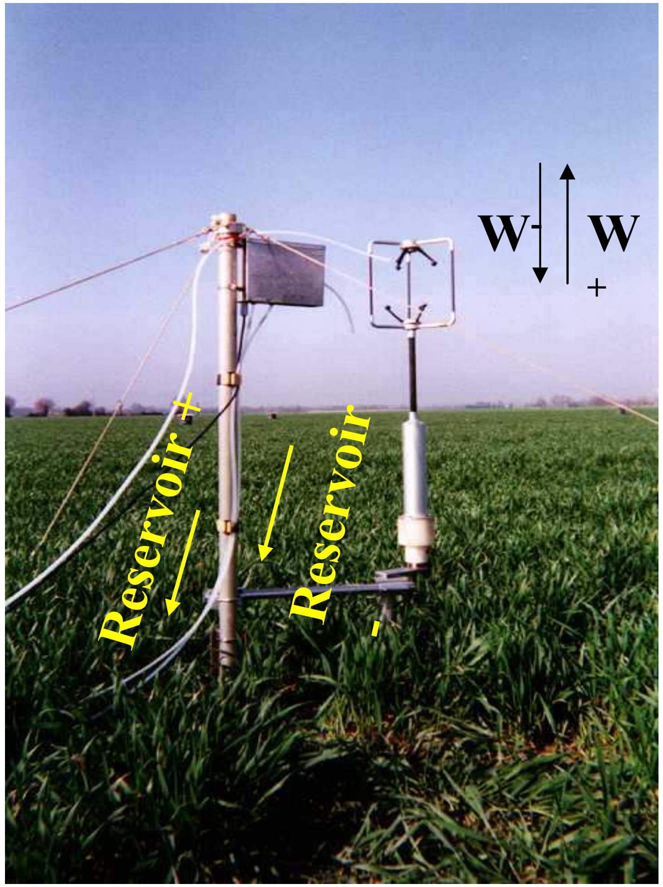
Air accumulation in 2 reservoirs (10 min)

Reservoirs air analysis (2 min)

Reservoirs emptying(3 min)

Flow is proportionnal to the concentration difference between the 2 reservoirs and to the standard deviation of the vertical speed ($\sigma_w$)

$$F_c = \beta \times \sigma_W \times \left(c^+ - c^-\right)$$

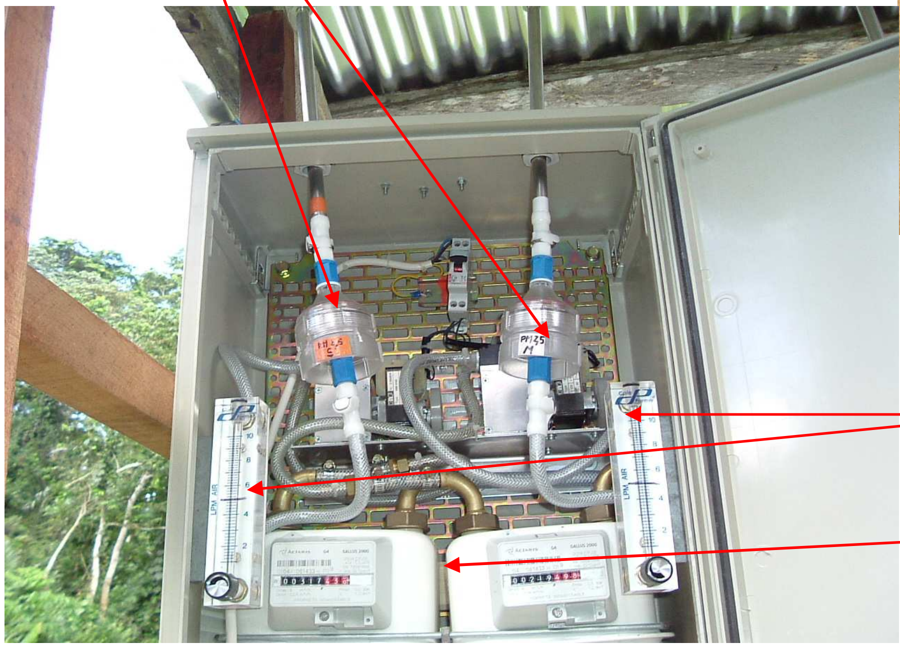


# Dry deposition: aerosols

## IDAF Sampling system

PM sampling inlet

Filters holders (pumps are behind)



Flow meters

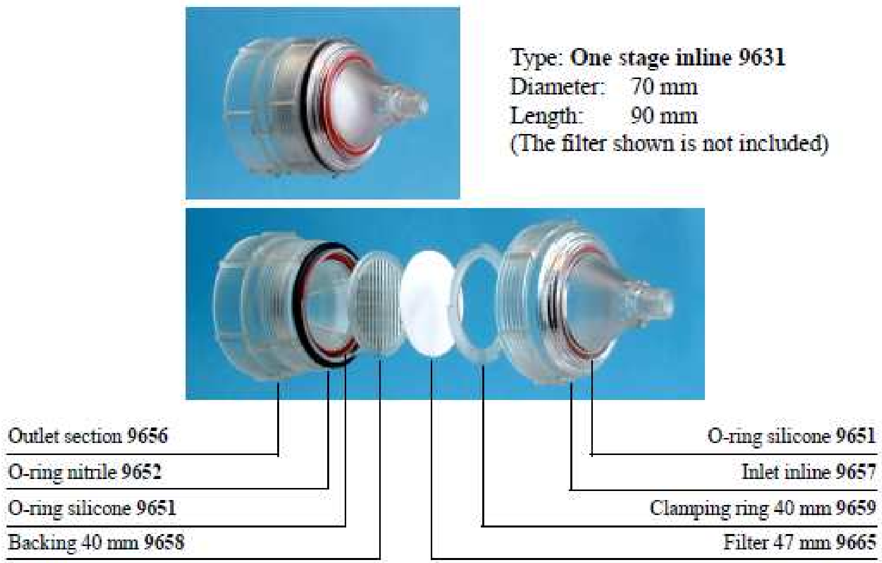
Gas counters

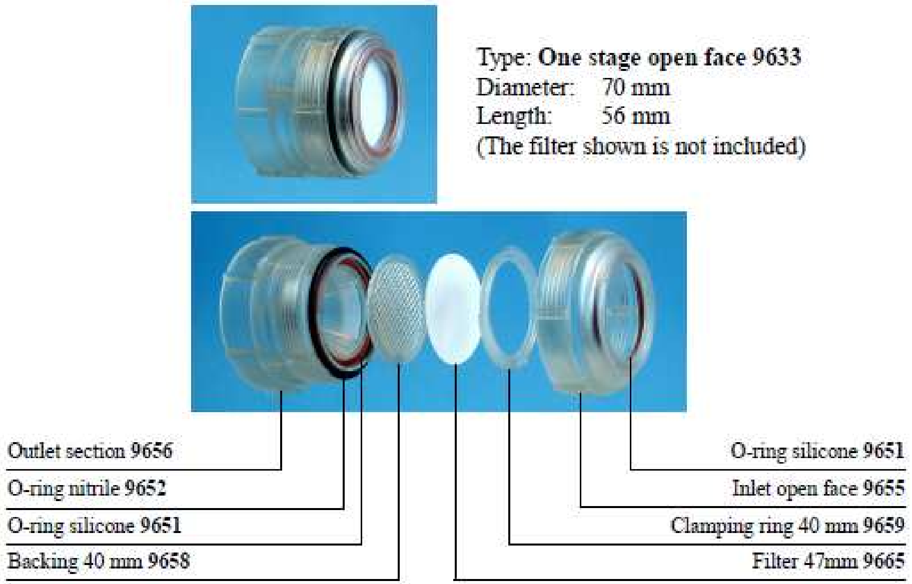
# Dry deposition: aerosols

Filter holders NILU for 47 mm filters

Inline: size segregation

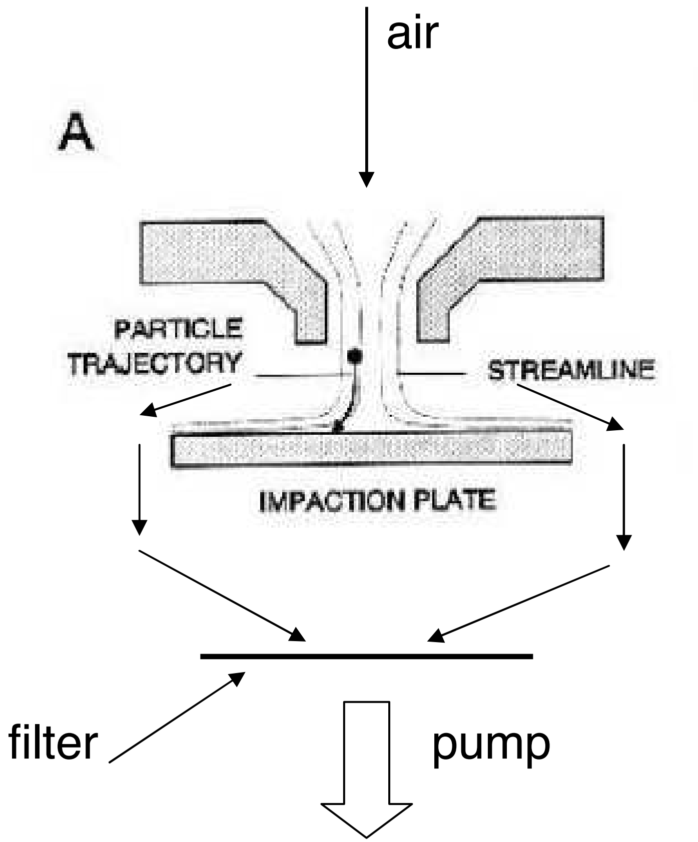
Open face: total



# Dry deposition: aerosols

## Size segregation: PM 2.5 and PM 10




47 mm filters used in NILU holders

Ions: 0.5$\mu$m Teflon Zefluor from Pall

Carbon: quartz QMA from Wathman

One week sampling period in sequential mode ( 15 min/h for example)

4 filters collected together ( PM 2,5 and PM 10 ; ions and carbon)

# Dry deposition: aerosols

Electrical Low Pressure Impactor: ELPI (DEKATI)
used for intensive measurement  periods : real time particle size distribution in the size range 7 nm-10 $\mu$m (13 stages cascade impactor)

Cascade impactor

Graphic user interface

# Dry deposition: aerosols

13 stages  cascade impactor (can be used alone with one pump)

| Stage | D50% [μm] |
|---|---|
| 13 | 10 |
| 12 | 6,8 |
| 11 | 4,4 |
| 10 | 2,5 |
| 9 | 1,6 |
| 8 | 1 |
| 7 | 0,65 |
| 6 | 0,4 |
| 5 | 0,26 |
| 4 | 0,17 |
| 3 | 0,108 |
| 2 | 0,06 |
| 1 | 0,03 |
| Filter stage | 0,007 |

Each impaction stage can be charged with 25 mm filters for chemical analysis

# Sample analysis back to lab

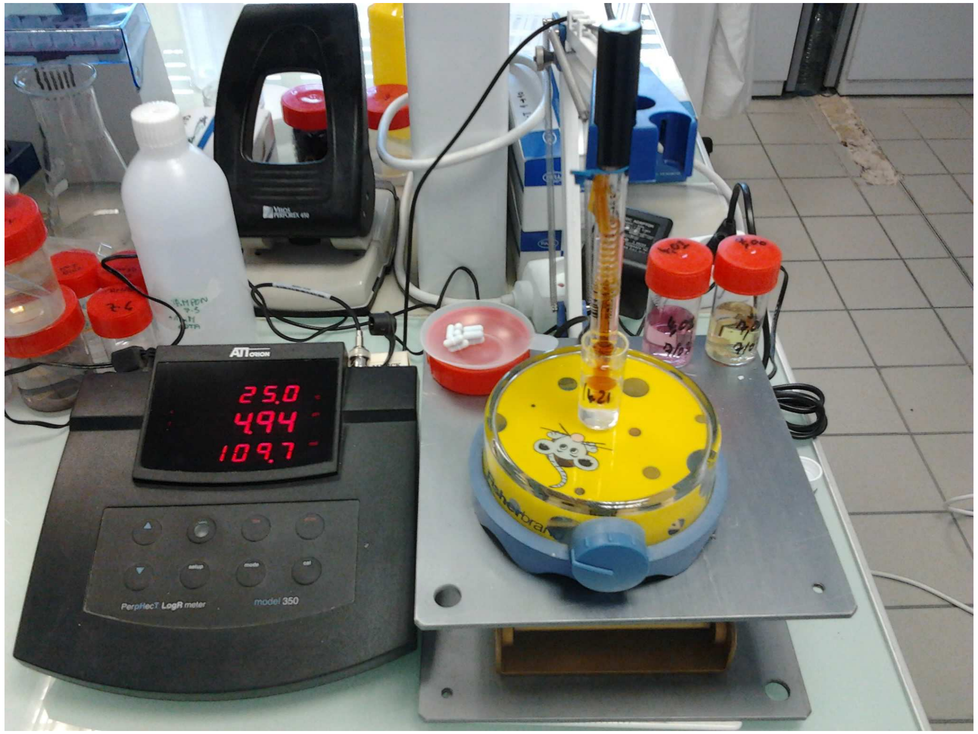
- Water system
- pH and conductivity
- Gravimetic analysis
- Ion Chromatography
- Thermal Optical analysis
- Thermal analysis
- ICP/ MS

# Water system

Type I ultra pure water:
(18.2 MΩ.cm;TOC< 5 ppb)
ELGA system
Eluent preparation,
standards dilution,
glassware cleaning and
samples soaking

# pH for rain samples

## Thermo Orion pH meter and electrode




Temperature compensated (25℃)

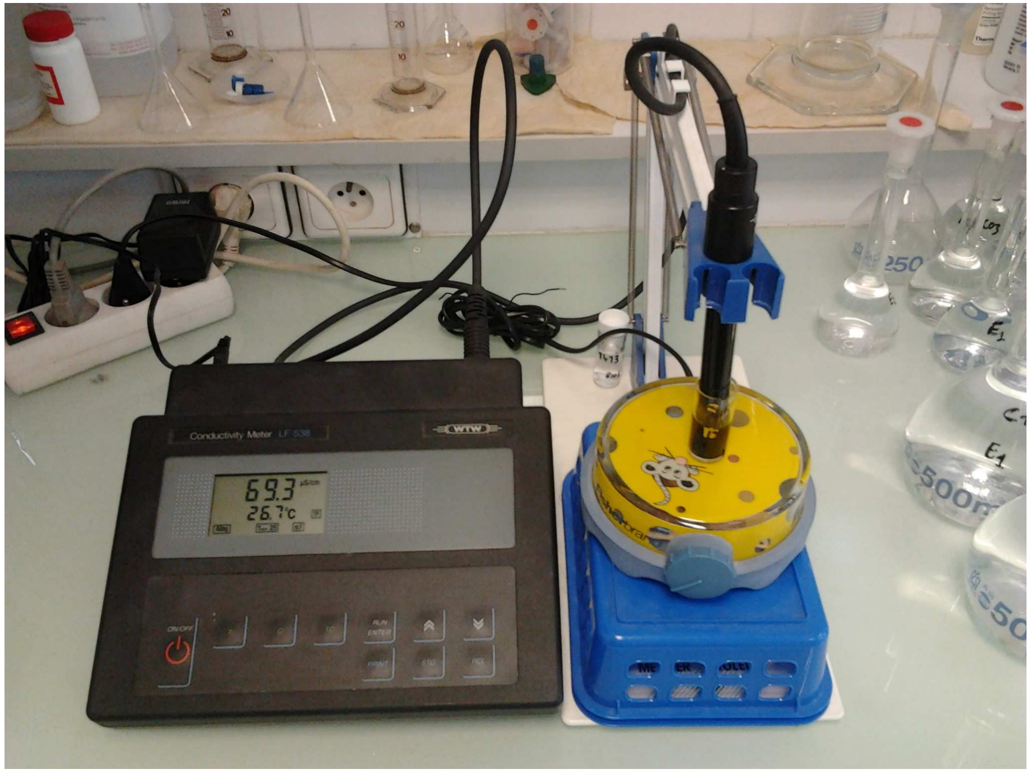
2 points calibration: 4,01 and 7,00

Match with majority of rain samples

Precision: +/- 0,01 pH

# Conductivity for rain samples

## WTW conductivity meter and sensor




Temperature compensated (25℃)

2 points calibration: 1413 and 23.8 $\mu$S

Precision: +/- 1.5%

# Gravimetric analysis

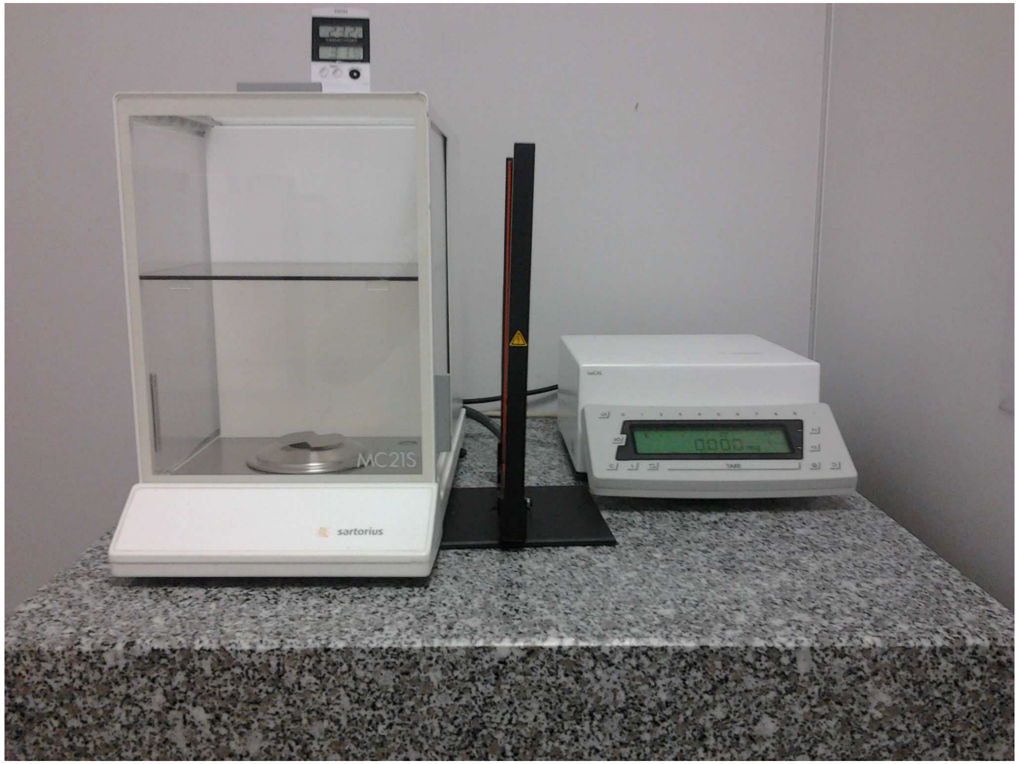
Teflon 47 or 25 mm filters weighted before and after collection

Sartorius MC 21S microbalance

+ Mettler Toledo

Anti-Electrostatic Generator

Precision: +/- 5 $\mu$g



# Ion Chromatography

- Rain samples: direct analysis
- Passive samplers: impregnated filters soaked in ultra pure water
- Aerosols samples: Teflon filters soaked in ultra pure water; 0.2 $\mu$m filtration if necessary. Only the soluble part available

# Ion Chromatography

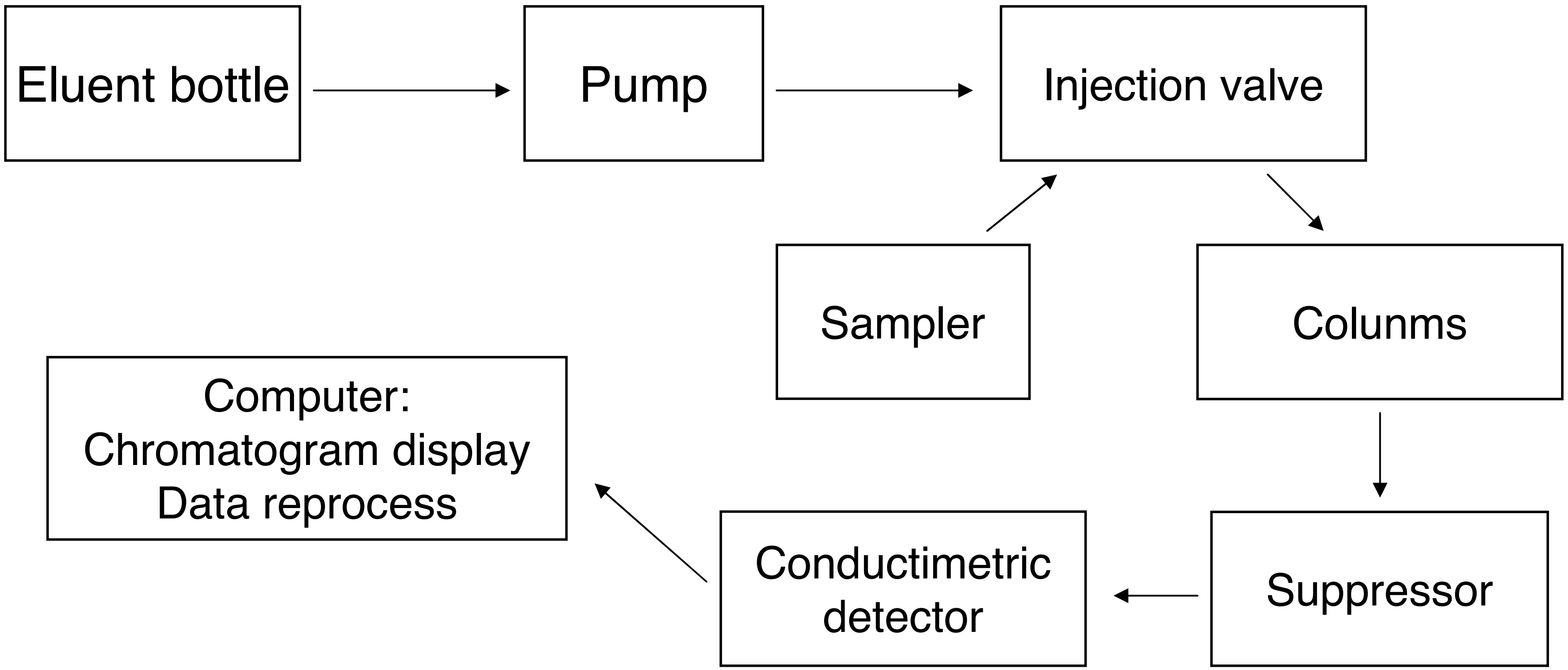
A part of HPLC, our systems from DIONEX

Specificities:

- ion-exchange columns (cations or anions)
- suppressed eluent before detector
- conductivity detector
- calibration by dilution of mono elemental standards
- detection limit: 10 ppb (10 $\mu$g/L)

# Ion Chromatography

## Schematic representation:



# Ion Chromatography

Cations analysis:

DIONEX ICS 1000

and automated sampler

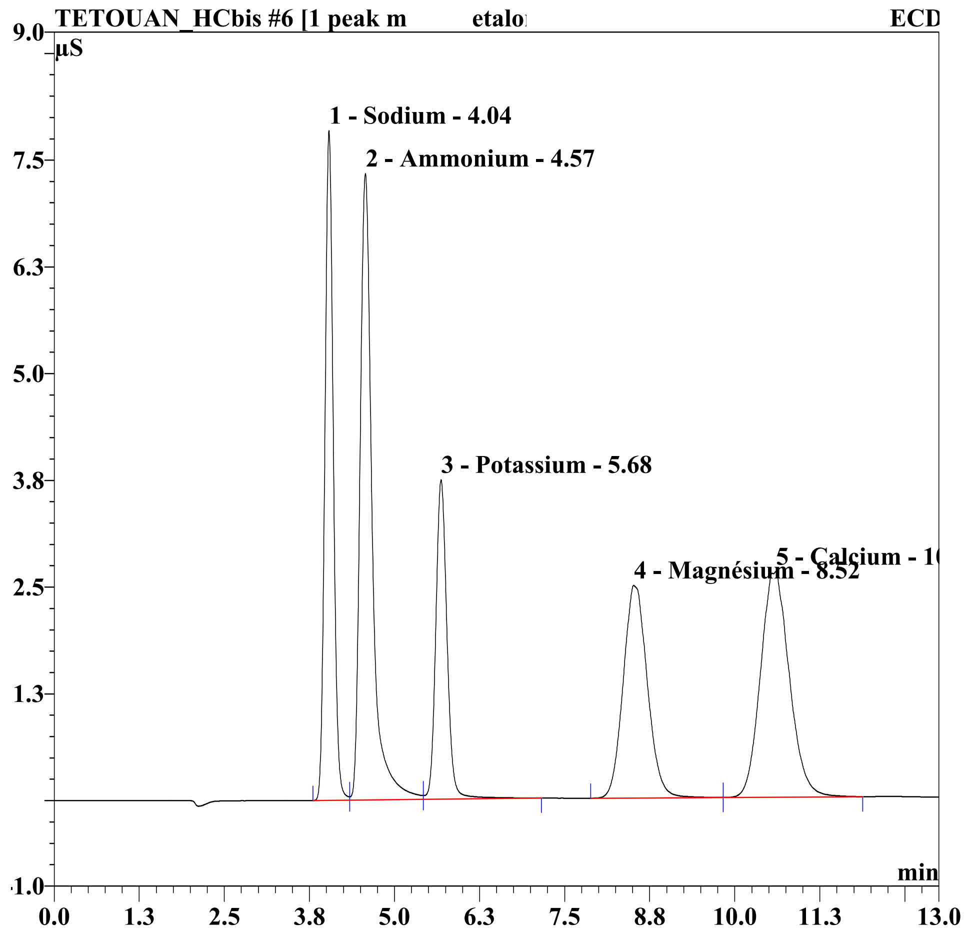
DIONEX AS50

# Ion Chromatography

Isocratic mode for majors inorganic cations:

Columns: CG12A+CS12A

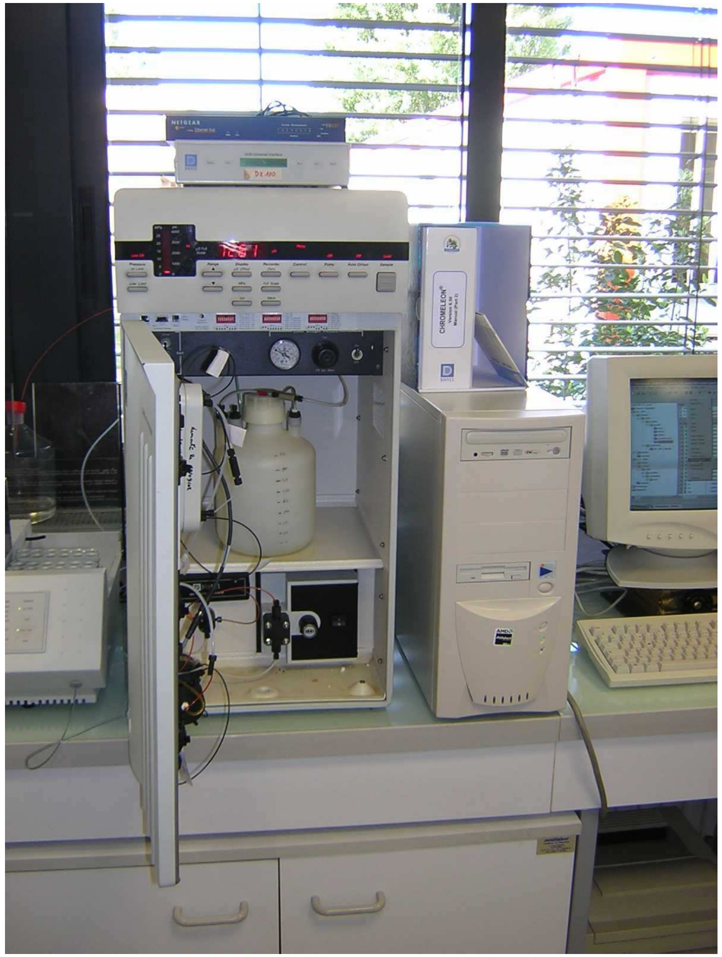
Eluent: 20 mM MSA (Methanesulfonic acid)



# Ion Chromatography

Mineral Anions analysis:
DIONEX DX100
and automated sampler
DIONEX AS 40

Mainly for passive samplers analysis

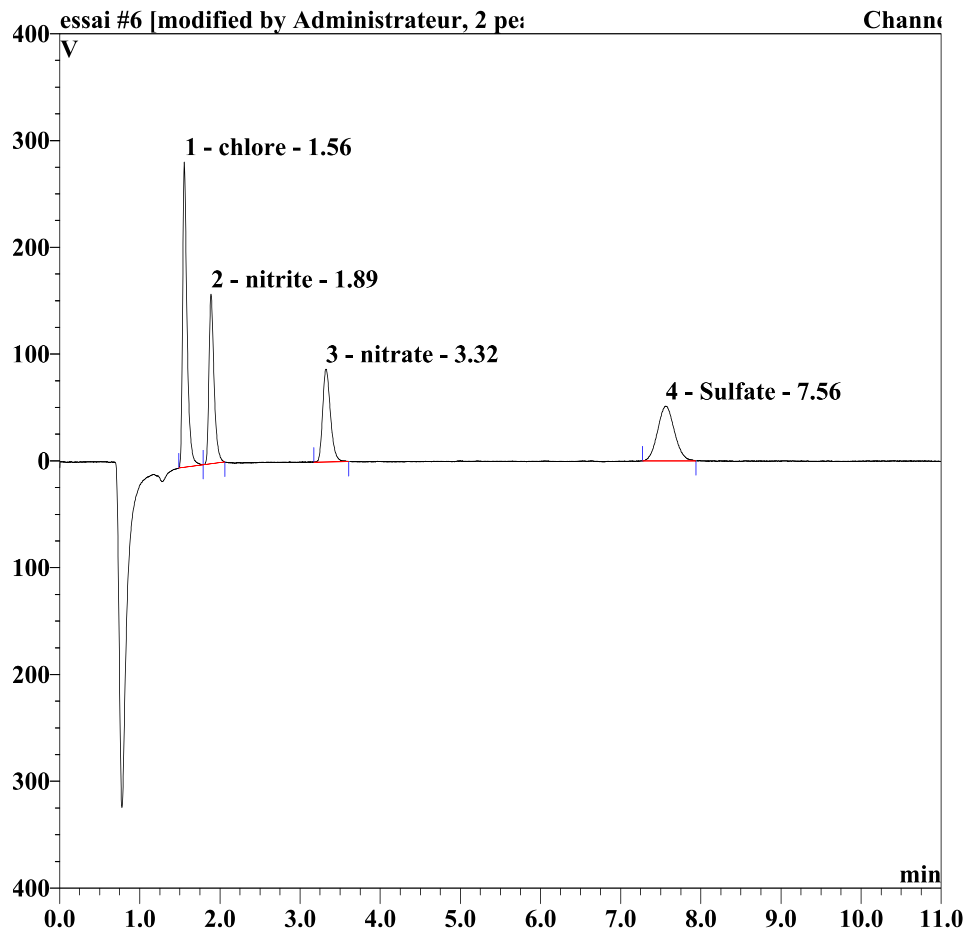


# Ion Chromatography

Isocratic mode for inorganic anions:

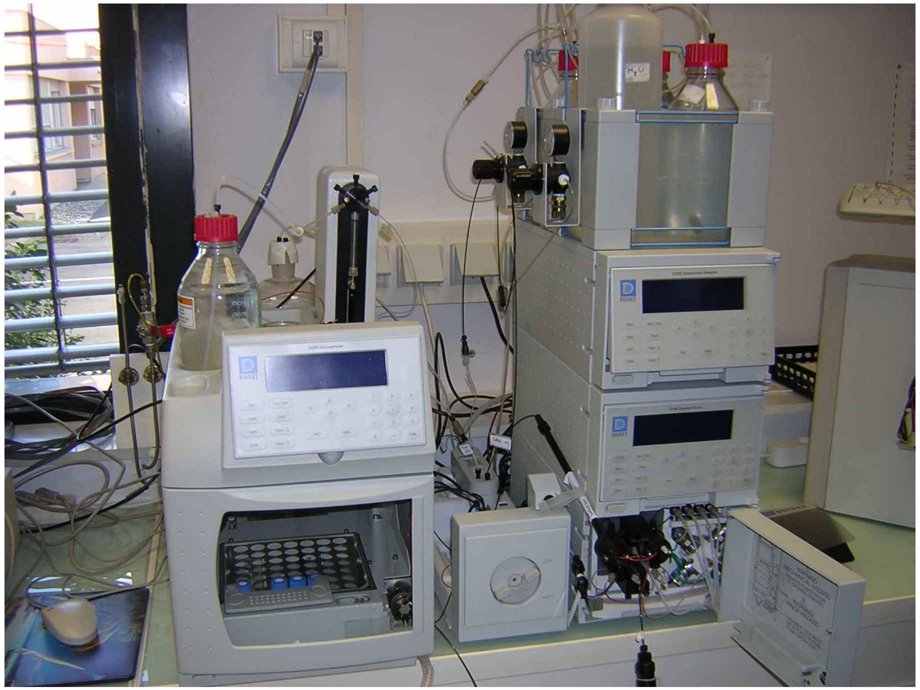
Columns: AG4A-SC+ AS4A-SC

Eluent :1.8mM $CO_3^{2-}$ /1.7 mM $HCO_3^-$



# Ion Chromatography

Anions analysis: DIONEX DX 500 and automated sampler AS50

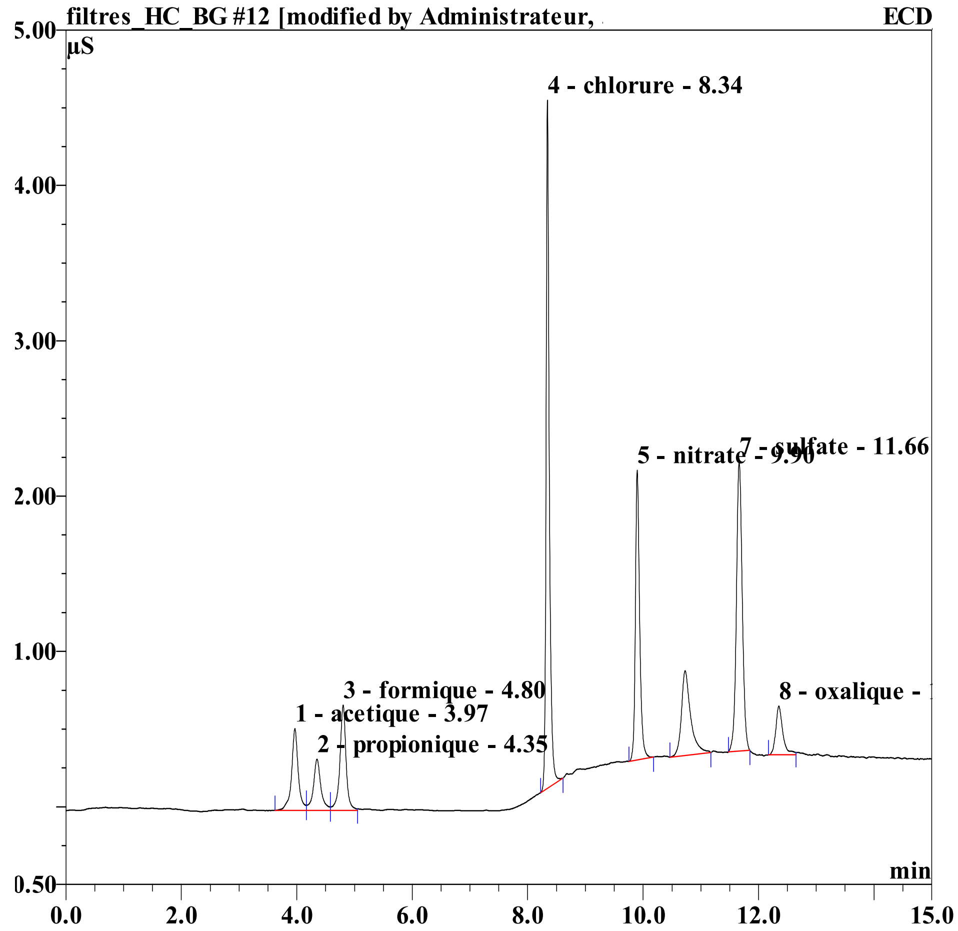


# Ion Chromatography

Gradient mode for small organic acids and inorganic anions in the same run

Columns: AG11+AS11

Eluent:0.4 mM NaOH to 8 mM NaOH



# Thermo optical analysis

DRI model 2001 carbon analyser

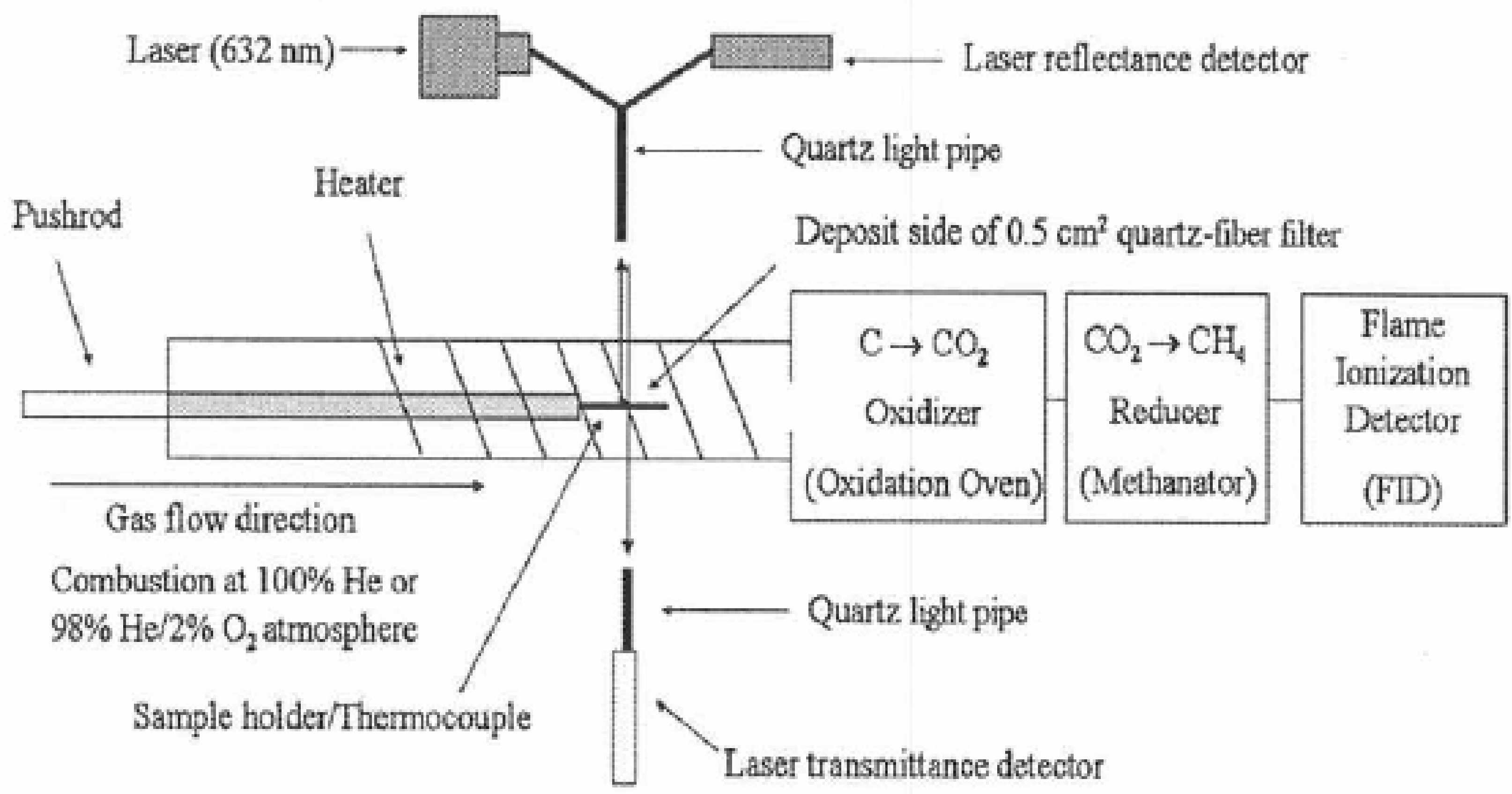

Quantify in the same run Organic Carbon and Black Carbon on an aerosol sample

TC = OC + BC

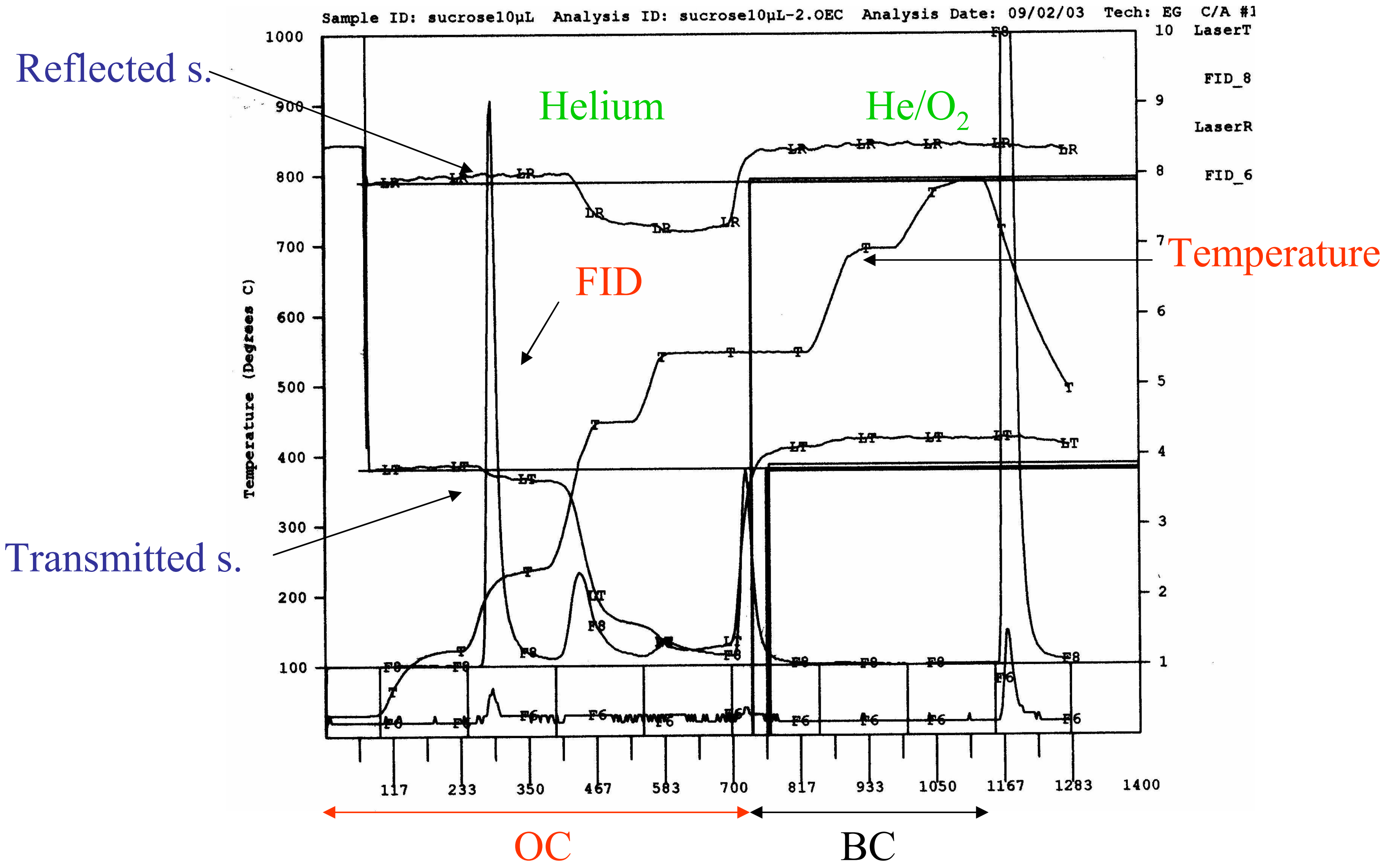
# Thermo optical analysis

- For quartz filters samples
- IMPROVE method used (Chow and Watson 2002)
- Calibration with methane and sucrose solutions
- Detection limit: 0.05 $\mu$g C/ $cm^2$

# Schematic representation



# Thermogram: IMPROVE method



# Thermal analysis

- Used with quartz filtrers
- Sample is heated to 1000℃ and $CO_2$ evolved is detected by infra-red
- Direct analysis of a sample : TC
- Sample heated 2 hours under oxygen flow to 340℃ before analysis : BC
- Then OC = TC - BC

# Thermal analysis

BRUKER

G4 ICARUS

Carbon Analyser

# ICP-MS

## Inductively coupled plasma mass spectrometry
## Located in GET laboratory

Fast analysis of a lot of elements (80)

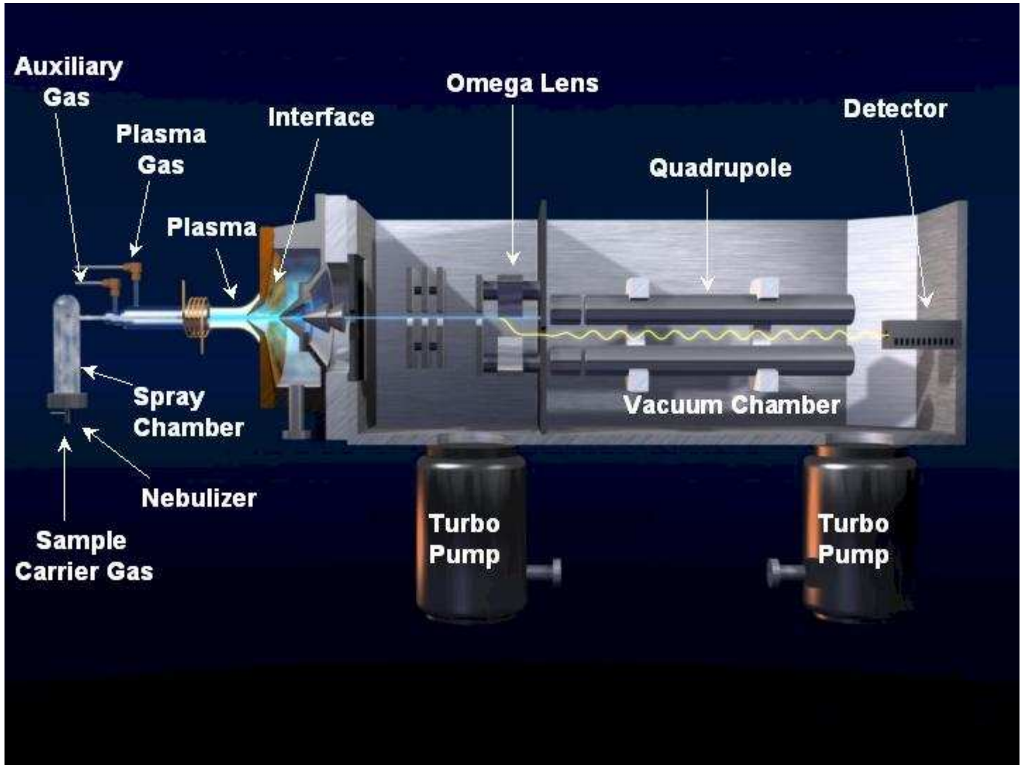
Includes isotopic speciation

Low detection limit 1 ppt ( 1 ng/L)

Acid attack on Teflon Filters in clean room

# ICP-MS

Thermo Finnigan system

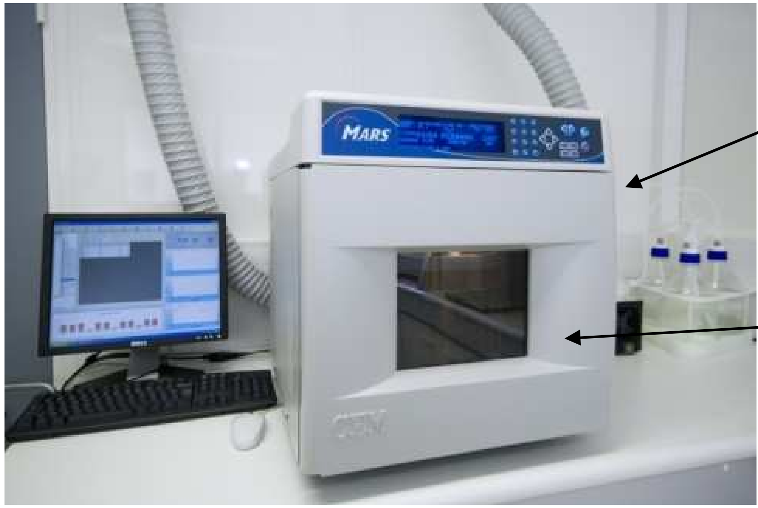



Schematic representation

# ICP-MS

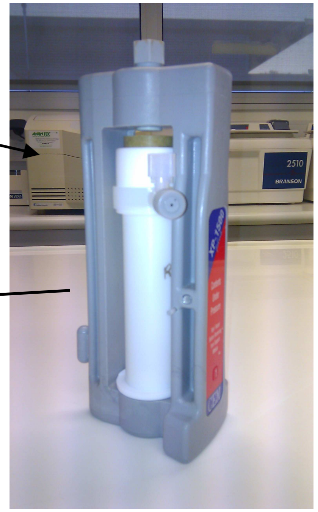
For TEFLON filters, method developped by our students for IDAF samples

- 10 ml nitric acid ($HNO_3$) bi-distilled + 0,5ml fluorhydric acid (HF)
- ultra-sonication for 15 minutes
- microwave digestion in two steps:
  15’ ramp until 160℃ hold 10 minutes
  10’ ramp until 180℃ hold 30 minutes
- rince with ultra pure water in the liner
- evaporate at 75℃ to dry , add 2% bi-distilled nitric ac id before ICP-MS analysis.




Micro-wave oven

Liner



# QA/QC

Quality Assurance in the sites:

- Enough sampling material available in the station (prevent lack)
- Procedures for changing of samples included in the field journal if there is changes in the technical staff
- Samples kept frozen just after collection (rain) or refrigerated (aerosols and passive samplers)
- Copies of sampling reporting forms should be sent to the lab (better than originals in case of loosing)
- Regular field blanks are necessary

# QA/QC

Quality assurance in the lab

- Daily calibration and check standards
- Standards mother solutions changed every year
- Standard operating procedures for each kind of samples
- Preventive maintenance for instruments
- Regular test of sampling materials :plastic bags, Greiner tubes, plastic glassware used for filters soaking, fresh prepared passive samplers and field blancks

# Quality Control

IDAF lab participates twice a year to the WMO/GAW intercomparison study: Analysis of 3 unknown simulated rain samples.

Parameters tested:

- pH, conductivity
- $Na^+$, $NH4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$
- $Cl^-$, $NO3^-$, $SO_4^{2-}$

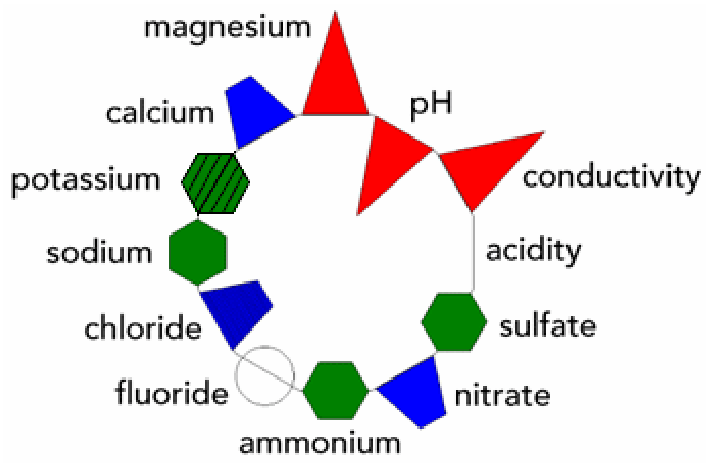
# Quality Control

## After WMO publishes statistics results and ring diagrams

**GOOD - Green Hexagon**
Measurement is within the interquartile range (IQR), defined as the 25th to 75th percentile or middle half (50%) of the measurements.
Examples: sulfate, ammonium, sodium, and potassium.

**SATISFACTORY - Blue Trapezoid**
Measurement is within the range defined by the median $\pm$ IQR/1.349. The ratio, IQR/1.349, is the non-parametric estimate of the standard deviation, sometimes called the pseudo-standard deviation.
Examples: nitrate, chloride, and calcium.

**UNSATISFACTORY - Red Triangle**
Measurement is outside the range defined by the median $\pm$ IQR/1.349.
Examples: pH, conductivity, and magnesium.



# Quality Control

**Precipitation**

**Chemistry**

**Data**

**Quality**

**Objectives**

| Measurement | DQO |
|---|---|
| pH | ± 0.07 units |
| conductivity | ± 7% |
| acidity | ± 25% |
| sulfate | ± 7% |
| nitrate | ± 7% |
| Ammonium | ± 7% |
| fluoride | none |
| chloride | ± 10% |
| sodium | ± 10% |
| potassium | ± 20% |
| calcium | ± 15% |
| magnesium | ± 10% |

# Sources

WMO/ GAW REPORT No 160 : MANUAL FOR THE GAW PRECIPITATION CHEMISTRY PROGRAMME:Data Quality Objectives and Standard Operating Procedures prepared by the GAW Precipitation Chemistry Science Advisory Group

Ferm and al. 1994. New mesurement technique for air pollutants(in swedish), Kemish tidskrift,1,30-32.

Chow, J.C., Watson, J.G., 2002. PM2.5 carbonate concentrations at regionally representative Interagency Monitoring of Protected Visual Environment sites. Journal of Geophysical Research 107 (D21), ICC6-1–ICC6-9. doi:10.1029/2001JD000574.

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| www.get.obs-mip.fr | www.nilu.no/products | www.dionex.com |
| http://idaf.sedoo.fr | www.thermoscientific.com | www.dri.edu |