



CCQM IAWG APRIL 2019

CCQM-P194: Number concentration of colloidal particles in solution

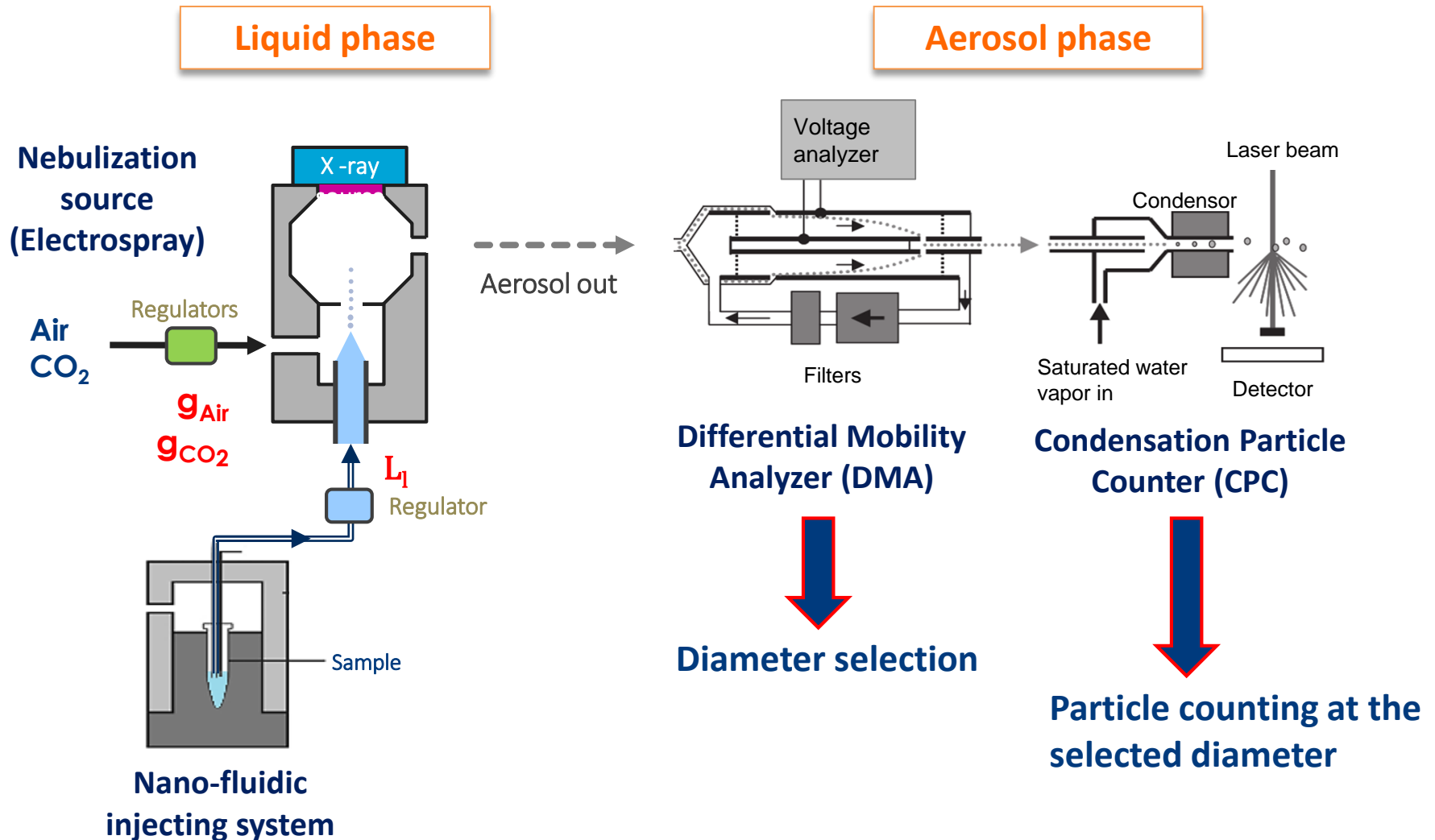
ES-DMA measurements

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8 April 2019

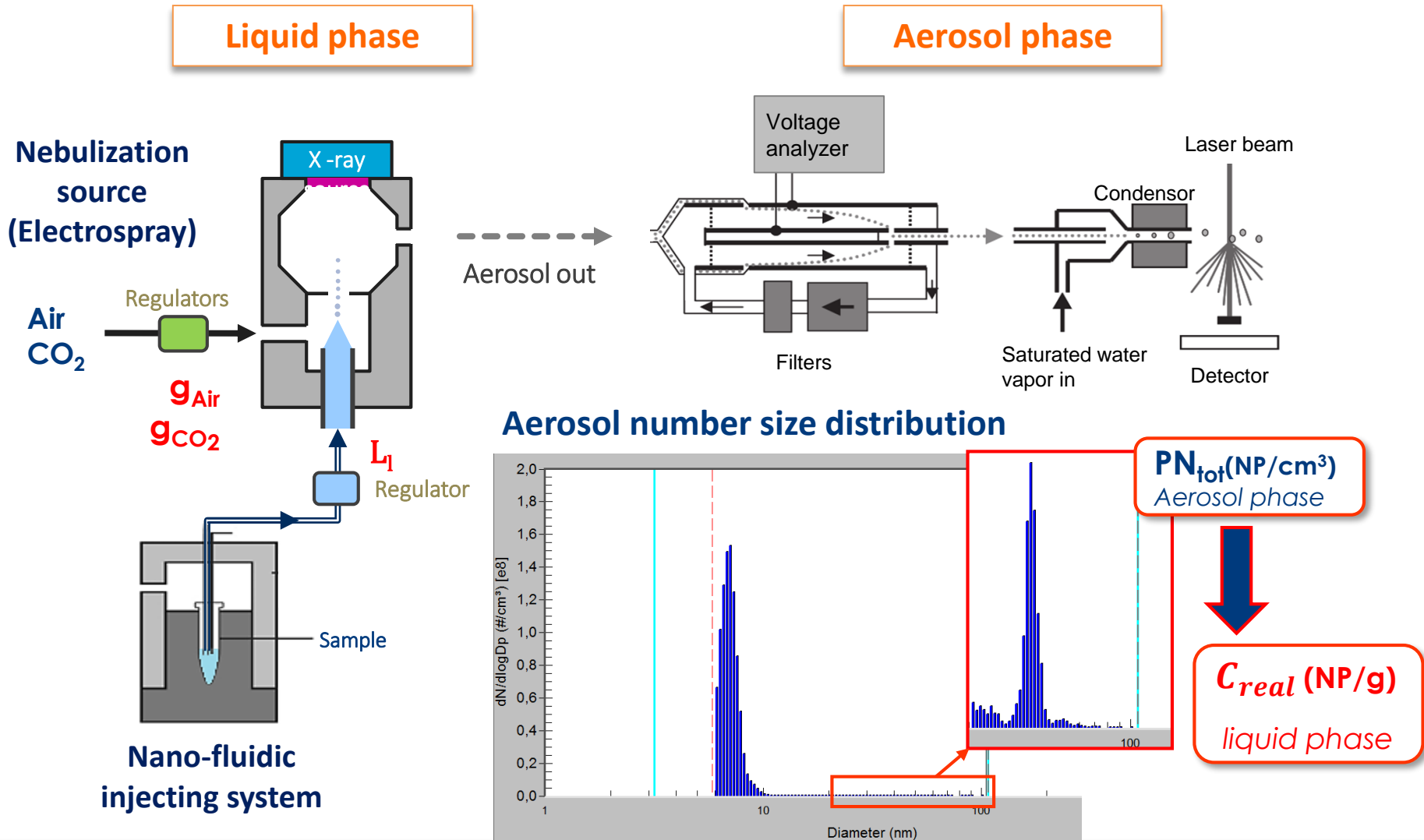
ELECTROSPRAY DIFFERENTIAL MOBILITY ANALYSIS (ES-DMA)

Principle



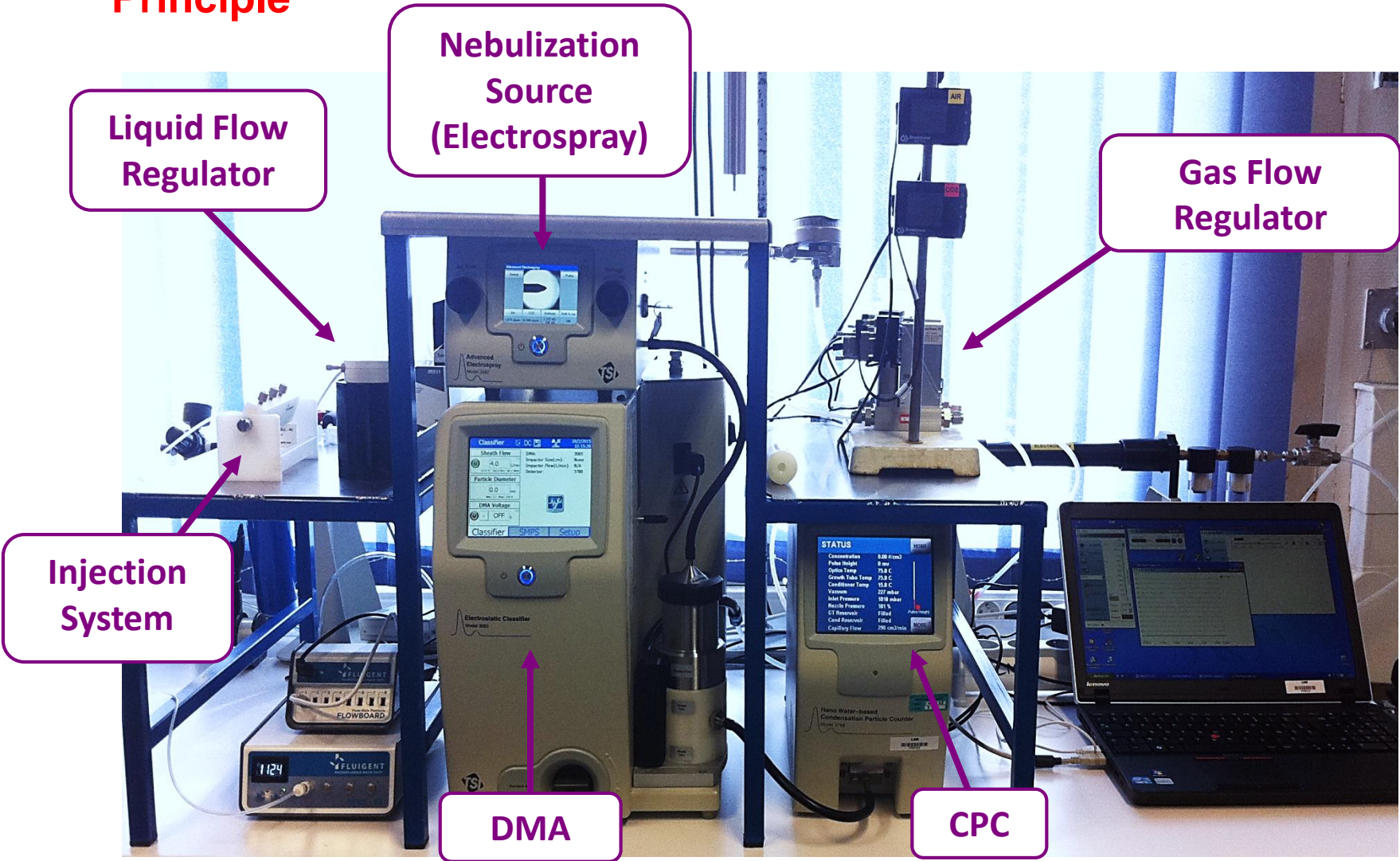
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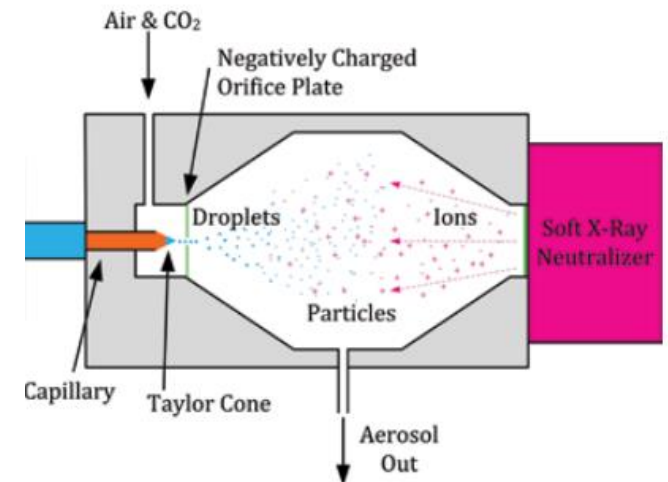
ELECTROSPRAY DIFFERENTIAL MOBILITY ANALYSIS (ES-DMA)

Sample and QC preparation

- Samples and QC (NIST RM 8012) stored in the fridge from reception until analysis (2 months)
- Return to room temperature before opening and used within one day after opening
- Aerosolization by electrospaying

➔ Formation of a Taylor cone due to the application of a high voltage to a conductive liquid exiting a capillary

➔ Gravimetric dilution of samples and QC in a high conductivity buffer (20mM Ammonium Acetate)



ELECTROSPRAY DIFFERENTIAL MOBILITY ANALYSIS (ES-DMA)

Post-analytical data processing

Particle concentration in the liquid sample, C_{real} :

$$C_{real} = PN_{tot} \times \frac{g_{AIR} + g_{CO_2}}{L_l \times E_{daily}} \times m \times \frac{1}{\rho}$$

The diagram illustrates the calculation of the real particle concentration in the liquid sample, C_{real} . The equation is enclosed in a red rounded rectangle. Arrows point from descriptive text boxes to the corresponding variables in the equation:

- Injected air flow rate** points to g_{AIR} .
- Injected CO₂ flow rate** points to g_{CO_2} .
- Dilution factor** points to m .
- Matrix (water) density** points to ρ .
- Total aerosol number concentration (peak integration)** points to PN_{tot} .
- Injected liquid flow rate** points to L_l .
- Daily electrospray transmission efficiency** points to E_{daily} .

ELECTROSPRAY DIFFERENTIAL MOBILITY ANALYSIS (ES-DMA)

Post-analytical data processing – aerosol phase PN_{tot}

Particle concentration in the liquid sample, C_{real} :

$$C_{real} = PN_{tot} \times \frac{g_{AIR} + g_{CO_2}}{L_l \times E_{daily}} \times m \times \frac{1}{\rho}$$

The diagram illustrates the calculation of the real particle concentration in the liquid sample, C_{real} . The equation is presented in a red-bordered box. Each variable in the equation is linked by an arrow to a descriptive label in a separate box:

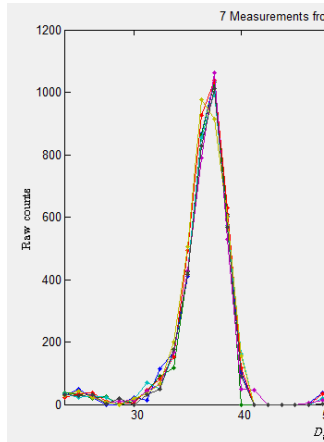
- PN_{tot} (Total aerosol number concentration (peak integration))
- $g_{AIR} + g_{CO_2}$ (Injected air flow rate + Injected CO_2 flow rate)
- $L_l \times E_{daily}$ (Injected liquid flow rate × Daily electrospray transmission efficiency)
- m (Dilution factor)
- ρ (Matrix (water) density)

Step 1 : processing of the number size distribution to obtain the aerosol phase particle concentration

ELECTROSPRAY DIFFERENTIAL MOBILITY ANALYSIS (ES-DMA)

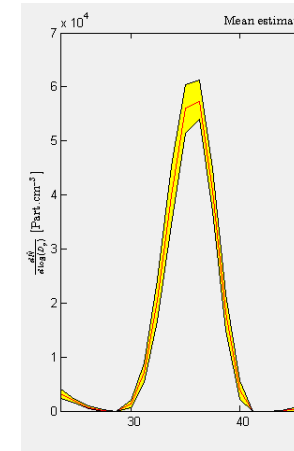
Post-analytical data processing – aerosol phase PN_{tot}

Raw aerosol number size distributions



In-house software

Mean number size distribution and associated standard deviation calculated on the basis of Monte-Carlo simulations



➔ Determination of PN_{tot} by peak integration

Coquelin *et al.*, 2015

ELECTROSPRAY DIFFERENTIAL MOBILITY ANALYSIS (ES-DMA)

Post-analytical data processing – daily electro spray transmission efficiency E_{daily}

$$C_{real} = PN_{tot} \times \frac{g_{AIR} + g_{CO_2}}{L_l \times E_{daily}} \times m \times \frac{1}{\rho}$$

Daily electro spray transmission efficiency

Step 2 : Determination of E_{daily}

$$E_{daily} = \frac{C_{ES-DMA}^{QC}}{C_{Certificate}^{QC}}$$

- Yield of aerosolized particles later measured by the SMPS system
- Made daily before sample analysis
- Calculated as the ratio between QC measured concentration and QC concentration from the certificate

ELECTROSPRAY DIFFERENTIAL MOBILITY ANALYSIS (ES-DMA)

Post-analytical data processing – daily electrospray transmission efficiency E_{daily}

$$E_{daily} = \frac{C_{ES-DMA}^{QC}}{C_{Certificate}^{QC}}$$

- $C_{Certificate}^{QC}$ RM 8012

| Measurement | Value |
|--|--------------|
| Au mass fraction ($\mu\text{g g}^{-1}$) ^(b) | 48.17 ± 0.33 |



$$C_{Certificate}^{QC} = 2.47 \times 10^{+11} \pm 1.25 \times 10^{+10} \text{ NP/g}$$

- $C_{ES-DMA}^{QC} = PN_{tot} \times \frac{g_{AIR} + g_{CO_2}}{L_l \times 1} \times m \times \frac{1}{\rho}$



- **Limited quantity of QC** (300 μ L), sufficient for only 3 days of measurements
- **QC not stable in ammonium acetate**, had to be used in less than an hour after preparation
- Time between QC/sample reception and analysis : 2 months
→ **Impact on QC ?**

ELECTROSPRAY DIFFERENTIAL MOBILITY ANALYSIS (ES-DMA)

Post-analytical data processing – daily electrospray transmission efficiency E_{daily}

$$C_{real} = PN_{tot} \times \frac{g_{AIR} + g_{CO_2}}{L_l \times E_{daily}} \times m \times \frac{1}{\rho}$$

$$0,75 < E_{daily} < 0,96$$

Key parameter in C_{real} determination

Step 3 : Determination of C_{real}

$$C_{real} = 1.18 \times 10^{11} \pm 1.71 \times 10^{10} \text{ NP/g} \\ (k=2)$$

Uncertainty budget :

