CCQM IAWG APRIL 2019

CCQM-P194: Number concentration of colloidal particles in solution

ES-DMA measurements

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ELECTROSPRAY DIFFERENTIAL MOBILITY ANALYSIS (ES-DMA)

Principle

Liquid phase

Aerosol phase

Nebulization source (Electrospray)

Air

\( g_{\text{Air}} \)

\( g_{\text{CO}_2} \)

Regulators

Sample

Nano-fluidic injecting system

X-ray

Differential Mobility Analyzer (DMA)

Voltage analyzer

Filters

Condensor

Detector

Saturated water vapor in

Laser beam

Diameter selection

Particle counting at the selected diameter
ELECTROSPRAY DIFFERENTIAL MOBILITY ANALYSIS (ES-DMA)

Principle

**Liquid phase**

**Aerosol phase**

Nebulization source (Electrospray)

Air

CO₂

\( g_{\text{Air}} \)

\( g_{\text{CO}_2} \)

\( L_1 \)

Regulator

Sample

Nano-fluidic injecting system

X-ray

Voltage analyzer

Filters

Condensor

Laser beam

Aerosol number size distribution

\[ \text{PN}_{\text{tot}}(\text{NP/cm}^3) \]  

Aerosol phase

\[ C_{\text{real}}(\text{NP/g}) \]  

liquid phase
ELECTROSPRAY DIFFERENTIAL MOBILITY ANALYSIS (ES-DMA)

**Principle**

- **Nebulization Source (Electrospray)**
- **Liquid Flow Regulator**
- **Injection System**
- **DMA**
- **Gas Flow Regulator**
- **CPC**
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 electrospraying

**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)**
Particle concentration in the liquid sample, $C_{\text{real}}$:

$$C_{\text{real}} = PN_{\text{tot}} \times \frac{g_{\text{AIR}} + g_{\text{CO}_2}}{L_1 \times E_{\text{daily}}} \times m \times \frac{1}{\rho}$$

- $PN_{\text{tot}}$: Total aerosol number concentration (peak integration)
- $g_{\text{AIR}}$: Injected air flow rate
- $g_{\text{CO}_2}$: Injected CO$_2$ flow rate
- $L_1$: Injected liquid flow rate
- $E_{\text{daily}}$: Daily electrospray transmission efficiency
- $m$: Dilution factor
- $\rho$: Matrix (water) density
ELECTROSPRAY DIFFERENTIAL MOBILITY ANALYSIS (ES-DMA)

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

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

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

- **Total aerosol number concentration (peak integration)**
- **Injected air flow rate**
- **Injected CO$_2$ flow rate**
- **Dilution factor**
- **Injected liquid flow rate**
- **Daily electrospray transmission efficiency**
- **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 $PN_{\text{tot}}$

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 $PN_{\text{tot}}$ by peak integration

Coquelin et al., 2015
ELECTROSPRAY DIFFERENTIAL MOBILITY ANALYSIS (ES-DMA)

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

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

Step 2: Determination of $E_{daily}$

- 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

$E_{daily} = \frac{C_{QC}^{ES-DMA}}{C_{QC}^{Certificate}}$
ELECTROSPRAY DIFFERENTIAL MOBILITY ANALYSIS (ES-DMA)

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

\[
E_{daily} = \frac{C_{QC}^{ES-\text{DMA}}}{C_{\text{Certificate}}^{QC}}
\]

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

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

- $C_{ES-\text{DMA}}^{QC} = PN_{tot} \times \frac{g_{\text{AIR}} + g_{\text{CO}_2}}{L \times L} \times m \times \frac{1}{\rho}$

  - Limited quantity of QC (300µL), 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 $E_{daily}$

$$C_{real} = PN_{tot} \times \frac{g_{AIR} + g_{CO_2}}{L_1} \times m \times \frac{1}{\rho}$$

$0.75 < E_{daily} < 0.96$

Step 3: Determination of $C_{real}$

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

Key parameter in $C_{real}$ determination

Uncertainty budget: