

Center for Aerosol In-Situ
European Center for Aerosol Calibration and Characterization

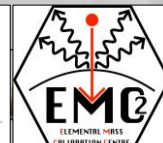
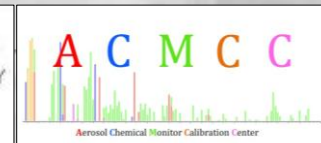


Charging, CPC & DMA - ITINERIS Training III

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EUROPEAN
REFERENCE
LABORATORY
FOR AIR
POLLUTION



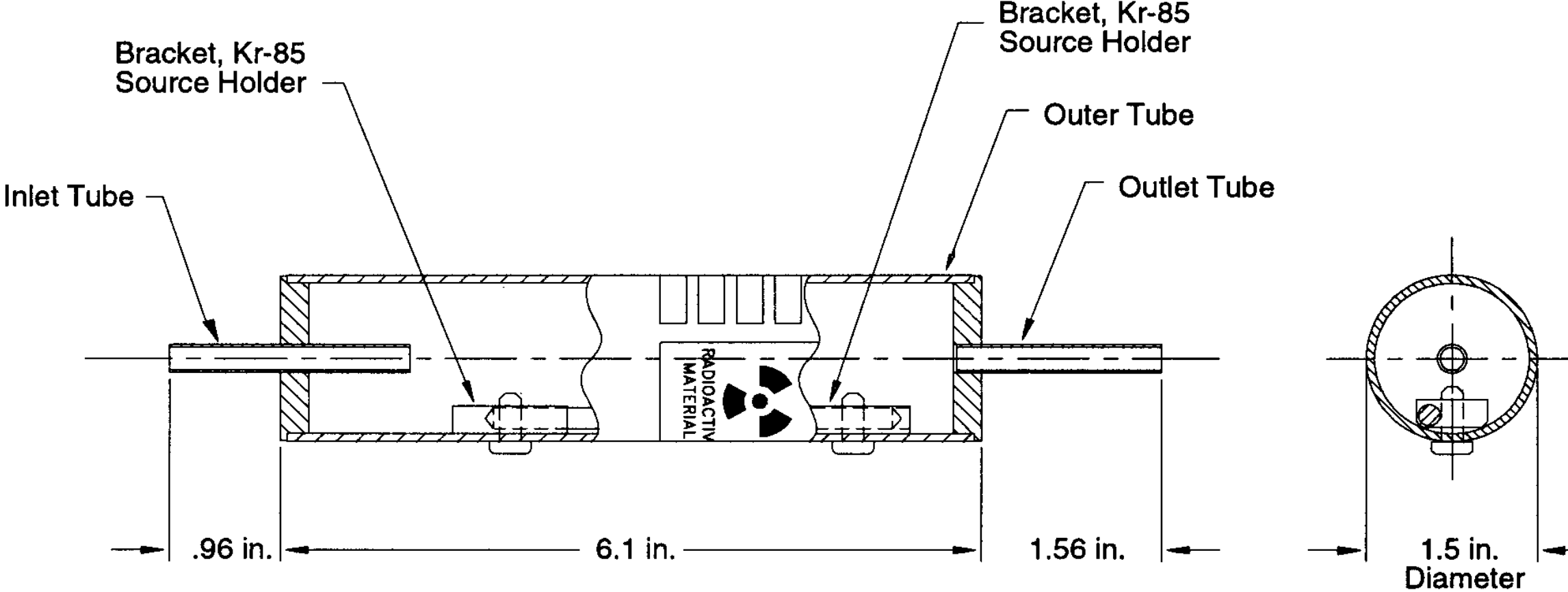
CCC
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Calibration
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Bipolar Charge Equilibrium

Bipolar Diffusion Charging

- Particles are charged by positive and negative gas ions.
- The ions are produced and transported to the particles in a neutralizer or bipolar diffusion charger.
- The ions are produced due to ionization of gas molecules by radioactive alpha or beta radiation or X-ray
- Kr^{85} , Am^{241} , Ni^{63} , Po^{210}
- The ions are transported to the particles surface due to
 - Diffusion → ion transport towards the particle by Brownian motion
 - Coulomb force → attracting or repulsing force due to charged particle
 - Force by Image charge → attracting force due to image charge in the particle

Example: Bipolar Charger TSI 3077A



(Manual: Neutralizer TSI 3077A)

Bipolar Charge Distribution - Equilibrium

- A single uncharged particle can be charged negatively by a negative ion at one moment.
- In the next moment, it can be neutralized by a positive ion.
- Each particle can be recharged several times during the bipolar charging process.
- The entire particle population, however, reaches a constant bipolar charge equilibrium with:
 - constant fractions of negatively and positively charged particles
 - constant fractions of uncharged, singly and multiple charged particles (size dependent)
- The different charge fractions of a certain particle size is constant (e.g., fraction of singly charged 100 nm particles).
- The fraction of negatively charged particles is greater than the fraction of positively charged particles (the mean mobility of negative ions is higher than the mobility of positive ions).

Bipolar Charge Distribution - Equilibrium

Advantages of the bipolar charge distribution

- time independent
- narrow for particles smaller than 300 nm
- known for the entire submicrometer size range
- simple to calculate

Disadvantages of the bipolar charge distribution

- broad for particles larger than 300 nm
- very low charging rate for particles smaller than 10 nm

Applications

- Particle number size distribution measurements
- generation of fine and ultrafine particles
- neutralization of highly charged particles

Gunn Charge Distribution

- The **Gunn bipolar charge distribution** takes the different electrical mobilities of positive and negative ions into account.
- The Gunn equation is however **only valid for particles larger than 100 nm** (mean free path of the ions much greater than the particle diameter).
- To describe the ion transport, the Gunn equation takes only the diffusion process into account.

$$F(n) = \frac{e}{\sqrt{4\pi^2 \cdot D_p \cdot k \cdot T}} \cdot \exp \left(- \frac{\left(n - \left(\frac{2\pi \cdot \epsilon_0 \cdot D_p \cdot k \cdot T}{e^2} \right) \ln \frac{N_{I+} \cdot Z_{I+}}{N_{I-} \cdot Z_{I-}} \right)^2}{\left(\frac{4\pi \cdot \epsilon_0 \cdot D_p \cdot k \cdot T}{e^2} \right)} \right)$$

Fuchs Charge Distribution

- The **Fuchs theory** describes the ion transport for the continuum and free molecular regime.
- Diffusion process as well as electrostatic forces between particles and ions are considered.
- The **Fuchs theory describes** the bipolar charge distribution for **the entire submicrometer particle size range**.
- There is **no analytical solution** for the Fuchs theory.
- The bipolar charge distribution is described by an approximation formula.
- This formula is used to calculate **the fraction of uncharged and singly charged particle in the size range 1-1000 nm**.
- The fraction of **doubly charged particle** can be calculated in the range **20-1000 nm**.

$$F(n) = 10^{\sum_{i=0}^5 a_i(n)(\log D_p / \text{nm})^i}$$

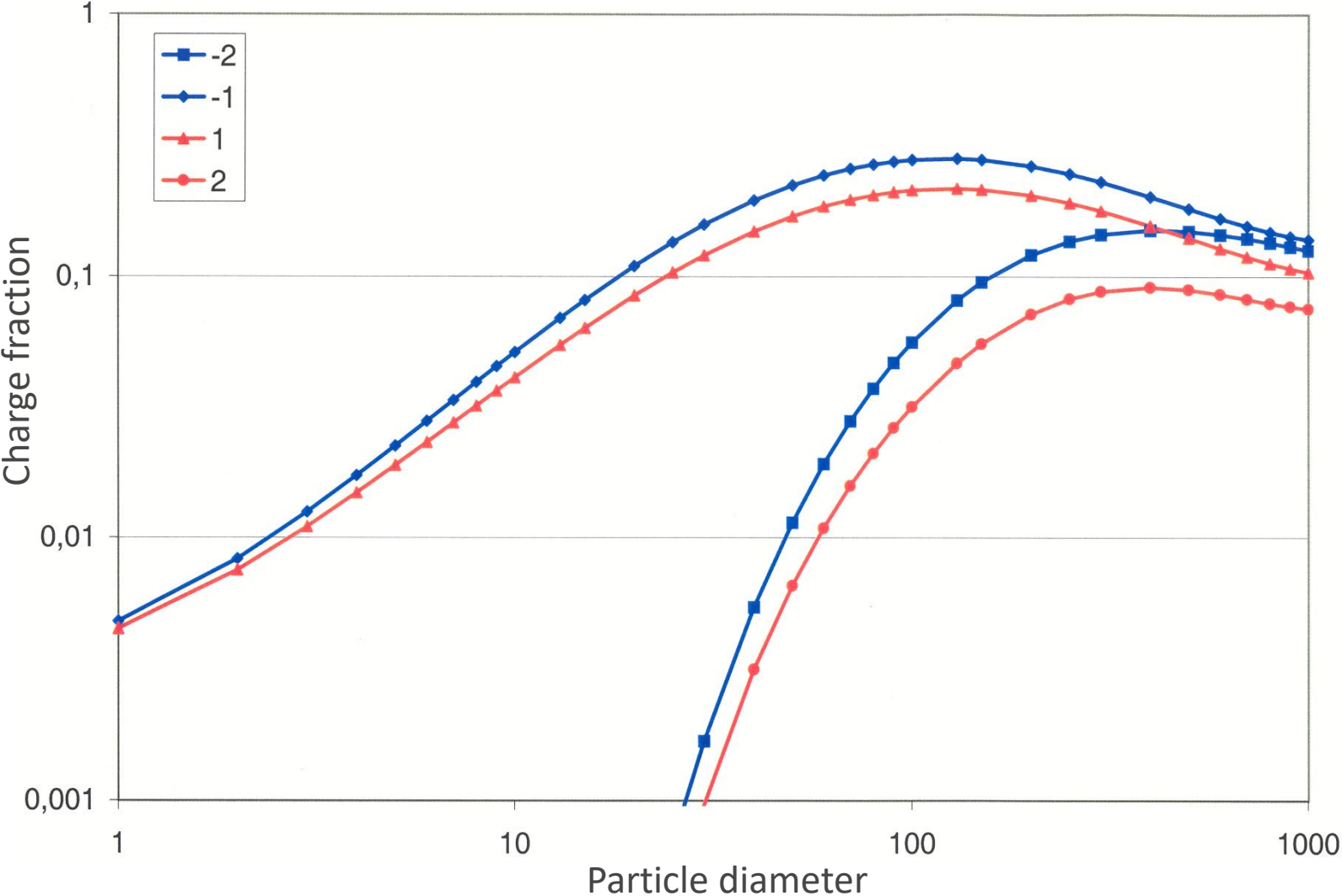
Approximation Coefficients

| | Approximation coefficients $a_i(n)$ | | | | |
|-----|-------------------------------------|---------|---------|---------|----------|
| i | $n=-2$ | $n=-1$ | $n=0$ | $n=+1$ | $n=+2$ |
| 0 | -26.3328 | -2.3197 | -0.0003 | -2.3484 | -44.4756 |
| 1 | 35.9044 | 0.6175 | -0.1014 | 0.6044 | 79.3772 |
| 2 | -21.4608 | 0.6201 | 0.3073 | 0.4800 | -62.8900 |
| 3 | 7.0867 | -0.1105 | -0.3372 | 0.0013 | 26.4492 |
| 4 | -1.3088 | -0.1260 | 0.1023 | -0.1553 | -5.7480 |
| 5 | 0.1051 | 0.0297 | -0.0105 | 0.0320 | 0.5049 |

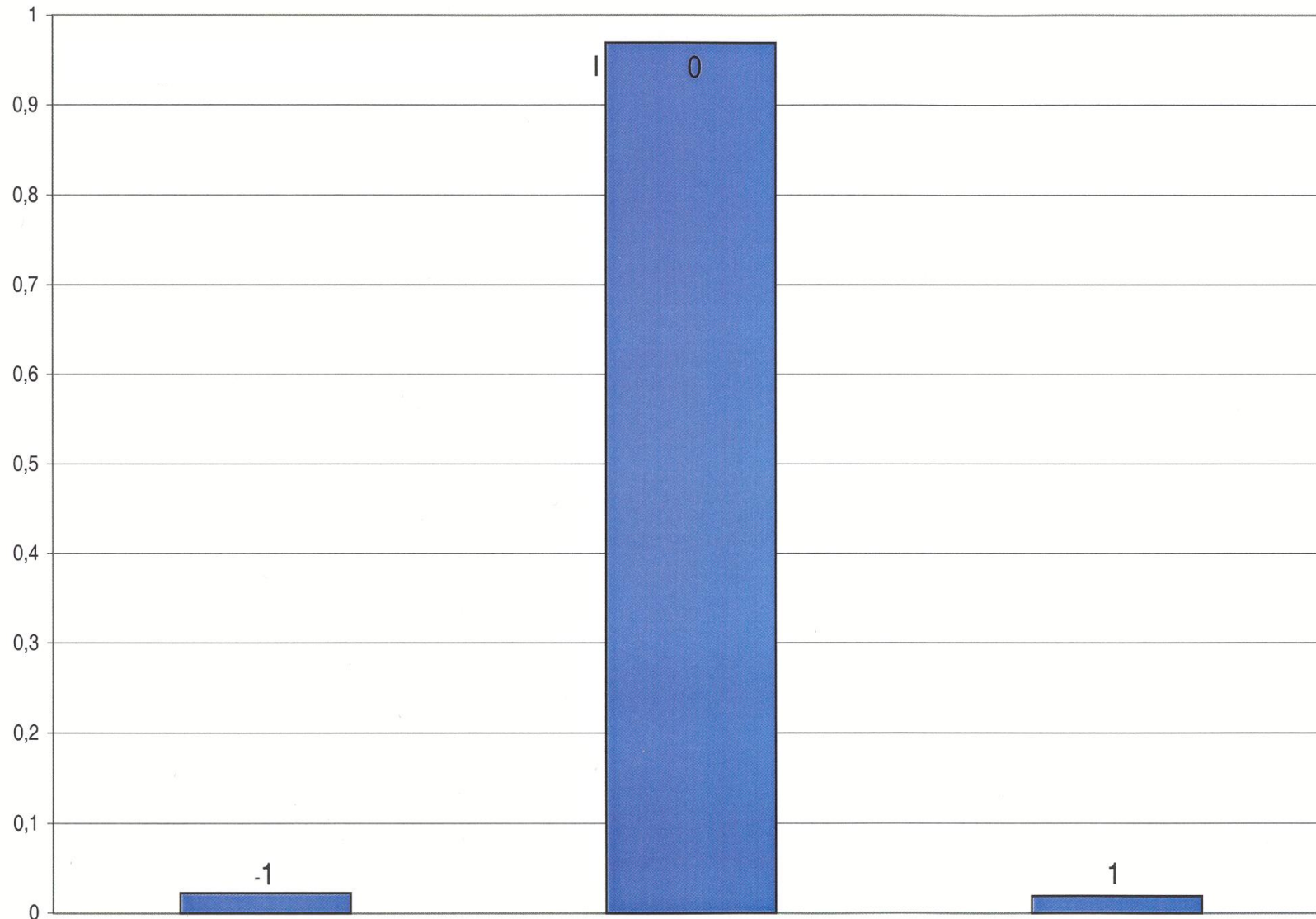
The fractions of multiple charged particles (-2, -1, 0, +1, +2) can be calculated using the approximation formula.

Wiedensohler, A. (1988). J. Aerosol Sci. 19, 387-389

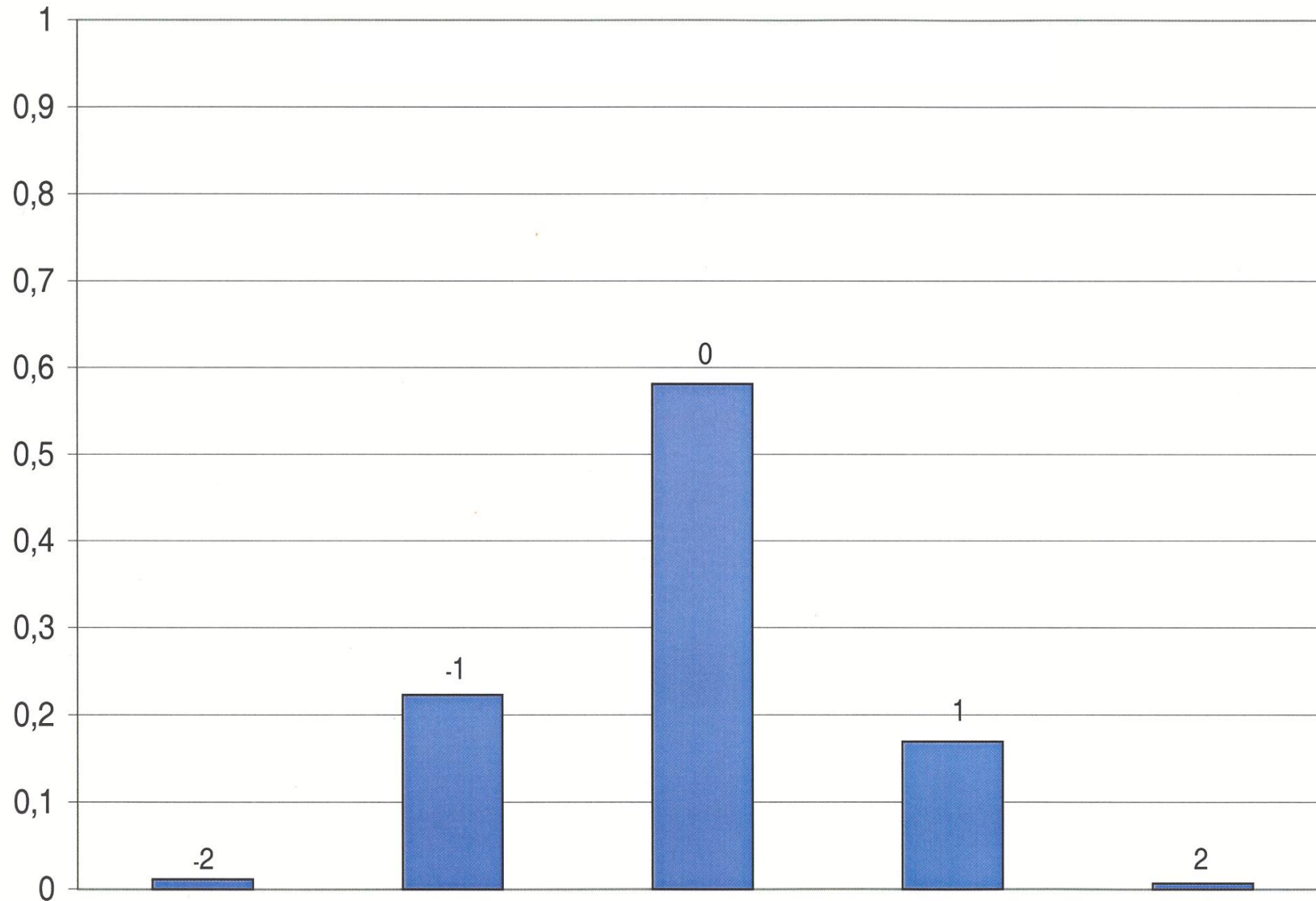
Bipolar Charge Distribution: Singly and Doubly Charged Particles



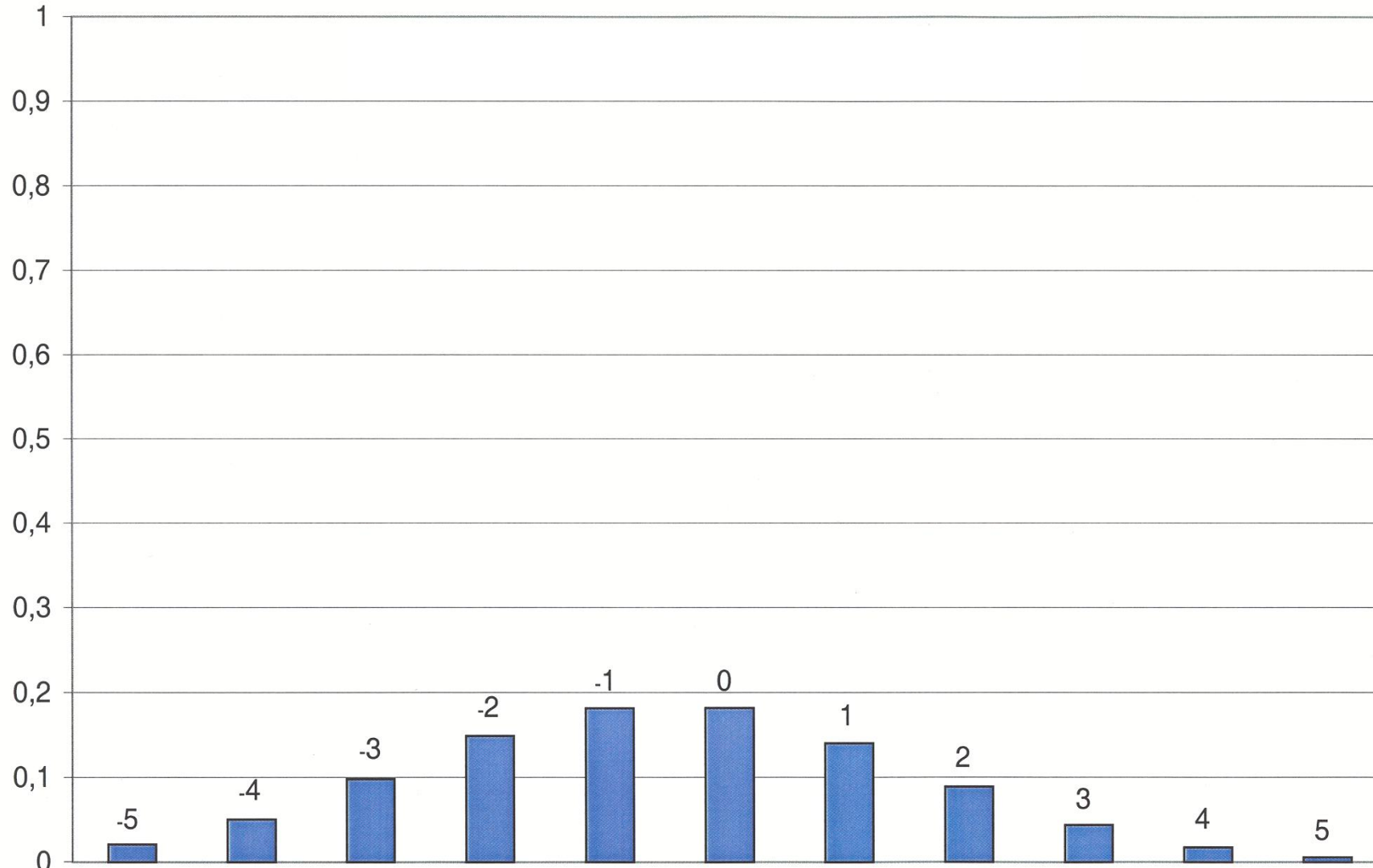
Bipolar Charge Distribution: 5 nm Particles



Bipolar Charge Distribution: 50 nm Particles



Bipolar Charge Distribution: 500 nm Particles



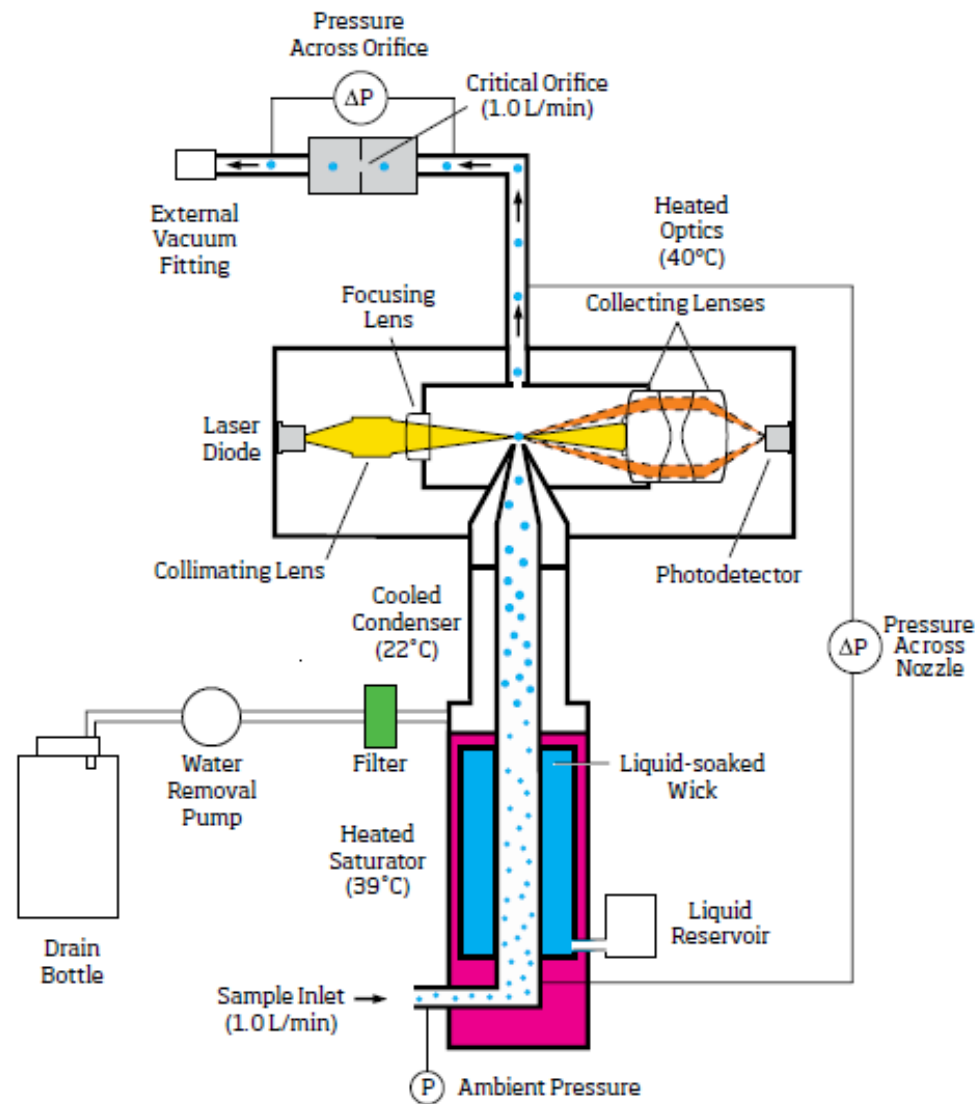
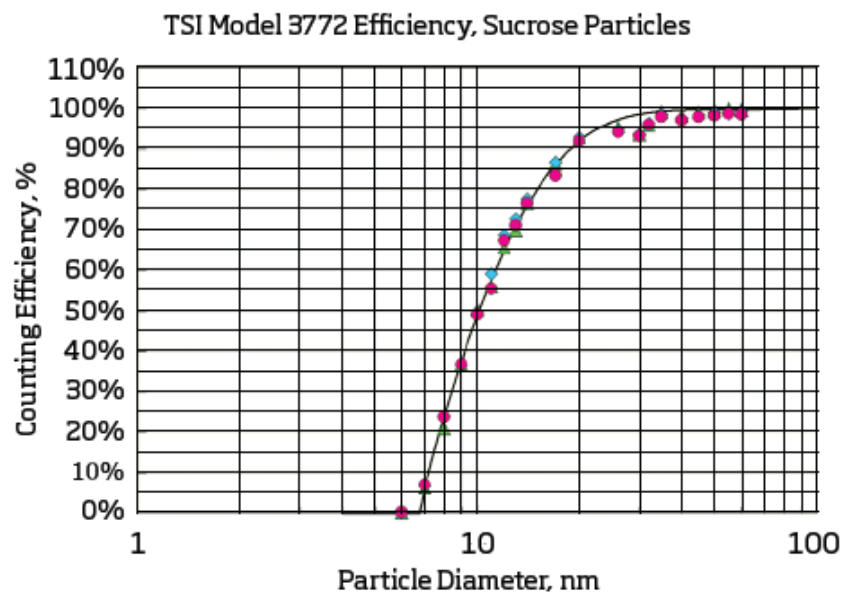
Charging, CPC & DMA - ITINERIS training IV

Bipolar Charge Distribution: Submicrometer Size Range

| Dp | -10 | -9 | -8 | -7 | -6 | -5 | -4 | -3 | -2 | -1 | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | sum |
|------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,00479 | 0,999309 | 0,004483 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1,008582 |
| 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,008287 | 0,974178 | 0,007514 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,989979 |
| 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,01254 | 0,976545 | 0,011019 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1,000103 |
| 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,017319 | 0,97513 | 0,014855 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1,007305 |
| 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,022491 | 0,969338 | 0,018936 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1,010765 |
| 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,027958 | 0,960507 | 0,023193 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1,011658 |
| 7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,03364 | 0,949754 | 0,027577 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1,010971 |
| 8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,039476 | 0,937844 | 0,032047 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1,009367 |
| 9 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,045416 | 0,92529 | 0,036568 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1,007274 |
| 10 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,051416 | 0,912431 | 0,041115 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1,004962 |
| 13 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,069473 | 0,873928 | 0,054707 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,998108 |
| 15 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,081332 | 0,849282 | 0,063585 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,994199 |
| 20 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,0002 | 0,109565 | 0,793069 | 0,084648 | 0,000101 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,987583 |
| 25 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,000696 | 0,135157 | 0,744591 | 0,103716 | 0,000387 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,984546 |
| 30 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,001681 | 0,157867 | 0,702788 | 0,120661 | 0,000966 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,983962 |
| 40 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,005419 | 0,195066 | 0,634651 | 0,148553 | 0,003141 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,98683 |
| 50 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3,11E-05 | 0,011424 | 0,222862 | 0,581445 | 0,169587 | 0,006552 | 1,4E-05 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,991915 |
| 60 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,000157 | 0,019157 | 0,243233 | 0,538606 | 0,185178 | 0,010879 | 7,05E-05 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,997281 |
| 70 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,000493 | 0,027975 | 0,257873 | 0,503249 | 0,196538 | 0,015794 | 0,000221 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1,002145 |
| 80 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,001154 | 0,037325 | 0,268121 | 0,473478 | 0,204626 | 0,02103 | 0,000518 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1,006252 |
| 90 | 0 | 0 | 0 | 0 | 0 | 0 | 3E-05 | 0,002217 | 0,04679 | 0,275007 | 0,447998 | 0,210188 | 0,026384 | 0,000995 | 1,03E-05 | 0 | 0 | 0 | 0 | 0 | 0 | 1,00962 |
| 100 | 0 | 0 | 0 | 0 | 0 | 0 | 7,84E-05 | 0,003719 | 0,056079 | 0,279319 | 0,425893 | 0,213796 | 0,03171 | 0,001669 | 2,69E-05 | 0 | 0 | 0 | 0 | 0 | 0 | 1,012289 |
| 130 | 0 | 0 | 0 | 0 | 0 | 1,24E-05 | 0,000564 | 0,01064 | 0,081327 | 0,282142 | 0,373956 | 0,216832 | 0,046649 | 0,004775 | 0,000194 | 0 | 0 | 0 | 0 | 0 | 0 | 1,017091 |
| 150 | 0 | 0 | 0 | 0 | 0 | 4,98E-05 | 0,001336 | 0,016745 | 0,095379 | 0,279019 | 0,347619 | 0,214917 | 0,055304 | 0,007515 | 0,000459 | 1,31E-05 | 0 | 0 | 0 | 0 | 0 | 1,018356 |
| 200 | 0 | 0 | 0 | 0 | 2,29E-05 | 0,000463 | 0,005275 | 0,033989 | 0,12113 | 0,264091 | 0,299086 | 0,204259 | 0,071865 | 0,015254 | 0,001812 | 0,000122 | 0 | 0 | 0 | 0 | 0 | 1,01737 |
| 250 | 0 | 0 | 0 | 0 | 0,000159 | 0,001716 | 0,011707 | 0,050601 | 0,136493 | 0,246477 | 0,265483 | 0,191075 | 0,082131 | 0,02271 | 0,004023 | 0,000451 | 3,21E-05 | 0 | 0 | 0 | 0 | 1,013059 |
| 300 | 0 | 0 | 0 | 5,5E-05 | 0,00057 | 0,004038 | 0,019563 | 0,064792 | 0,145008 | 0,229754 | 0,240558 | 0,178281 | 0,08781 | 0,029079 | 0,006722 | 0,001062 | 0,000115 | 0 | 0 | 0 | 0 | 1,007408 |
| 400 | 0 | 0 | 6,53E-05 | 0,000485 | 0,002711 | 0,011388 | 0,035967 | 0,085403 | 0,150602 | 0,202036 | 0,205575 | 0,15664 | 0,091014 | 0,038329 | 0,012359 | 0,002996 | 0,000546 | 7,48E-05 | 0 | 0 | 0 | 0,99619 |
| 500 | 0 | 5,91E-05 | 0,00036 | 0,001742 | 0,006718 | 0,02062 | 0,05038 | 0,097974 | 0,149 | 0,181581 | 0,181804 | 0,140331 | 0,089098 | 0,04397 | 0,017311 | 0,005425 | 0,001353 | 0,000269 | 4,25E-05 | 0 | 0 | 0,988037 |
| 600 | 4,69E-05 | 0,00025 | 0,0011 | 0,004006 | 0,012066 | 0,030045 | 0,061859 | 0,105306 | 0,144743 | 0,166668 | 0,164351 | 0,128212 | 0,085601 | 0,047261 | 0,021255 | 0,007904 | 0,00243 | 0,000618 | 0,00013 | 2,26E-05 | 0 | 0,983875 |
| 700 | 0,000167 | 0,000689 | 0,00241 | 0,00716 | 0,018074 | 0,038759 | 0,070618 | 0,109314 | 0,139729 | 0,155806 | 0,150849 | 0,119196 | 0,082039 | 0,04906 | 0,024265 | 0,010197 | 0,00364 | 0,001104 | 0,000285 | 6,23E-05 | 1,16E-05 | 0,983435 |
| 800 | 0,00043 | 0,00146 | 0,004293 | 0,010948 | 0,024206 | 0,046407 | 0,077146 | 0,1112 | 0,134759 | 0,147932 | 0,140006 | 0,112483 | 0,079024 | 0,049906 | 0,026508 | 0,012209 | 0,004876 | 0,001688 | 0,000507 | 0,000132 | 2,98E-05 | 0,986149 |
| 900 | 0,000889 | 0,002595 | 0,006669 | 0,015099 | 0,030118 | 0,052923 | 0,081922 | 0,111713 | 0,130165 | 0,142315 | 0,131047 | 0,107515 | 0,076776 | 0,050136 | 0,028149 | 0,013923 | 0,006066 | 0,002328 | 0,000787 | 0,000235 | 6,15E-05 | 0,991431 |
| 1000 | 0,001578 | 0,004081 | 0,009418 | 0,01939 | 0,035617 | 0,05837 | 0,085344 | 0,111328 | 0,126067 | 0,138452 | 0,123481 | 0,103896 | 0,075353 | 0,049963 | 0,029325 | 0,015356 | 0,007174 | 0,00299 | 0,001112 | 0,000369 | 0,000109 | 0,998771 |

Condensation Particle Counter

Sketch of a CPC TSI model 3772/3750



ACTRIS Recommendation Condensation Particle Counter

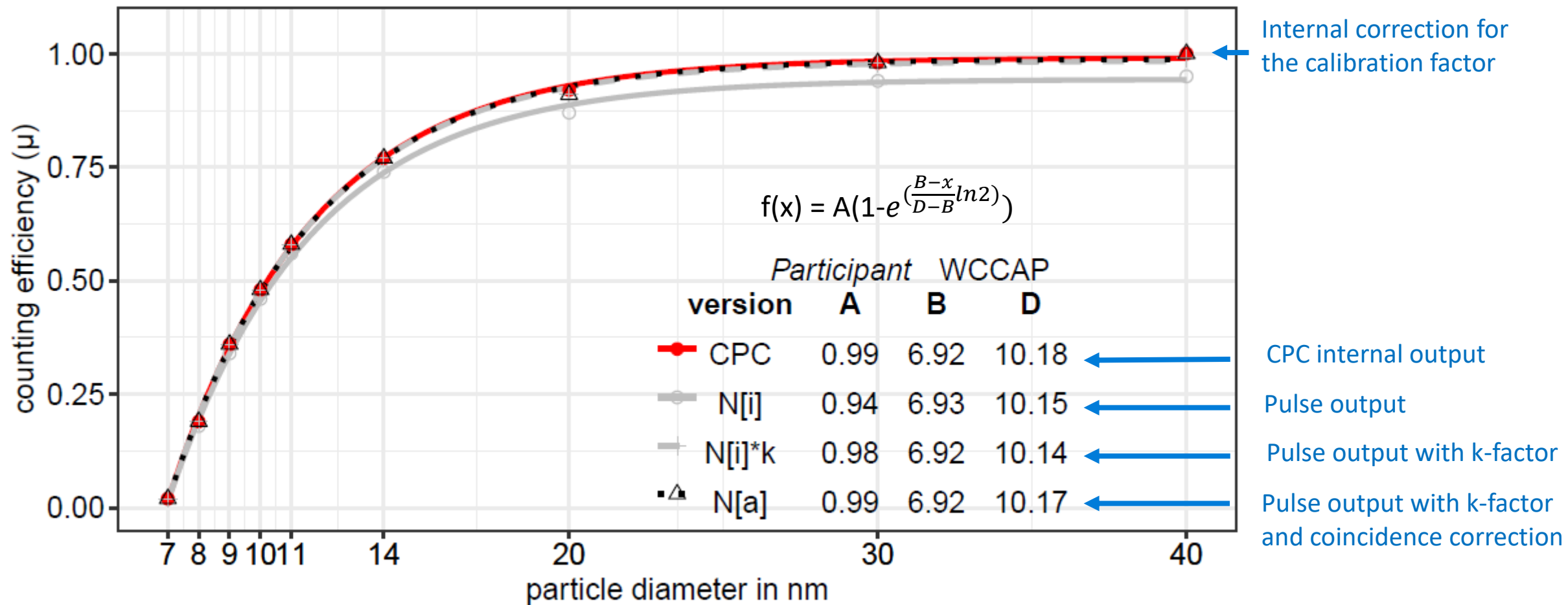
Condensation Particle Counter (CPC) - EN16976 – 10 nm

The EN 16976 recommends following:

- Full flow (inlet flow rate equal to detection flow rate)
- Butanol as working fluid
- $D_{P50} = 10 \text{ nm}$ (+/-10%)
- Pulse Output (raw data) plus USB or ethernet port (corrected data)
- Frequent calibration according specific criteria
- Calibration aerosol = monodisperse Silver Nano Particles (7 – 40 nm)
- Uncertainty after calibration factor & coincidence corrections +/-5%

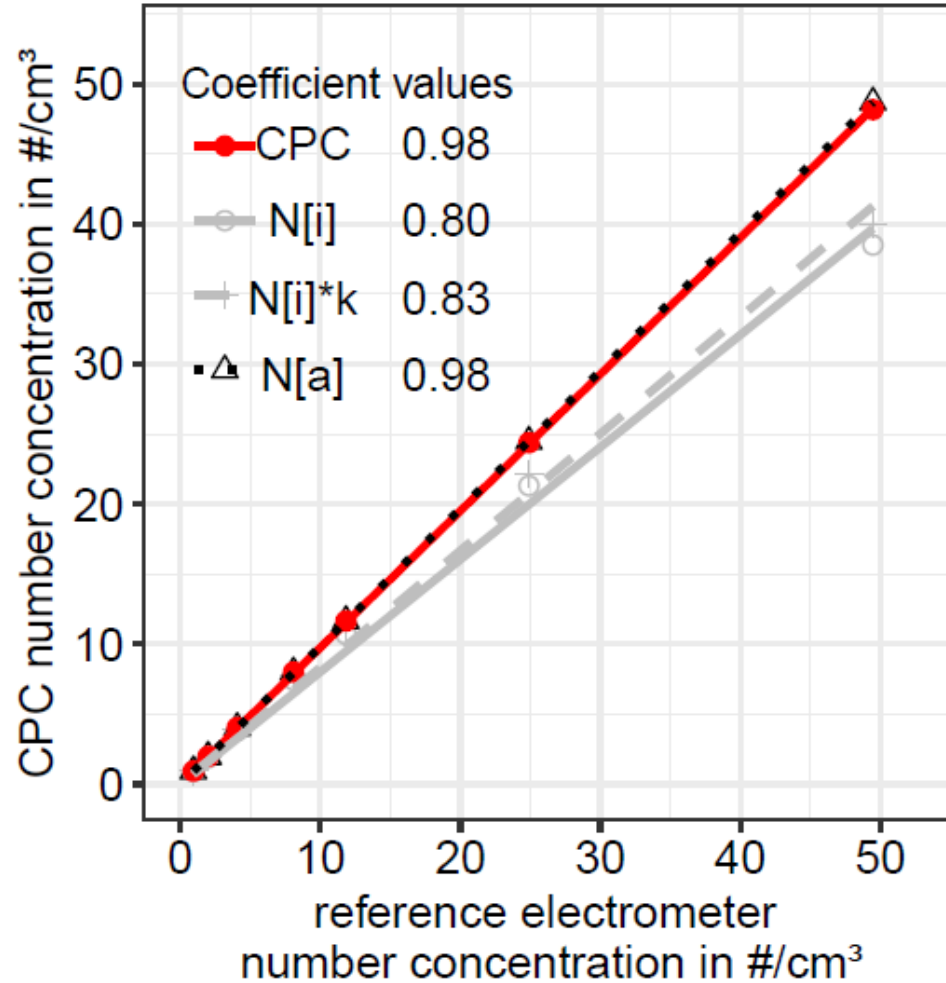
Condensation Particle Counter - Calibration

CPC Calibration – Detection Efficiency Curve



Example of a CPC Calibration – Linearity

Example TSI CPC 3750-10



$$N_a = k \left(\frac{1}{c^2} \left(\frac{1}{N_i} - c \right) - \sqrt{\left(\frac{1}{c^2} \left(\frac{1}{N_i} - c \right) \right)^2 - \frac{2}{c^2}} \right)$$

N_a = corrected concentrations (particles/cm³)

N_i = pulse concentrations (particles/cm³)

k = k-factor: 1.04 for TSI CPC model 3750-10

c = coincidence parameter: $4.2e^{-06}$

Example: TSI CPC model-specific parameter

Principle of a Differential Mobility Analyzer-

Electrical Particle Mobility

The mobility of aerosol particles in an electrostatic field is called electrical particle mobility.

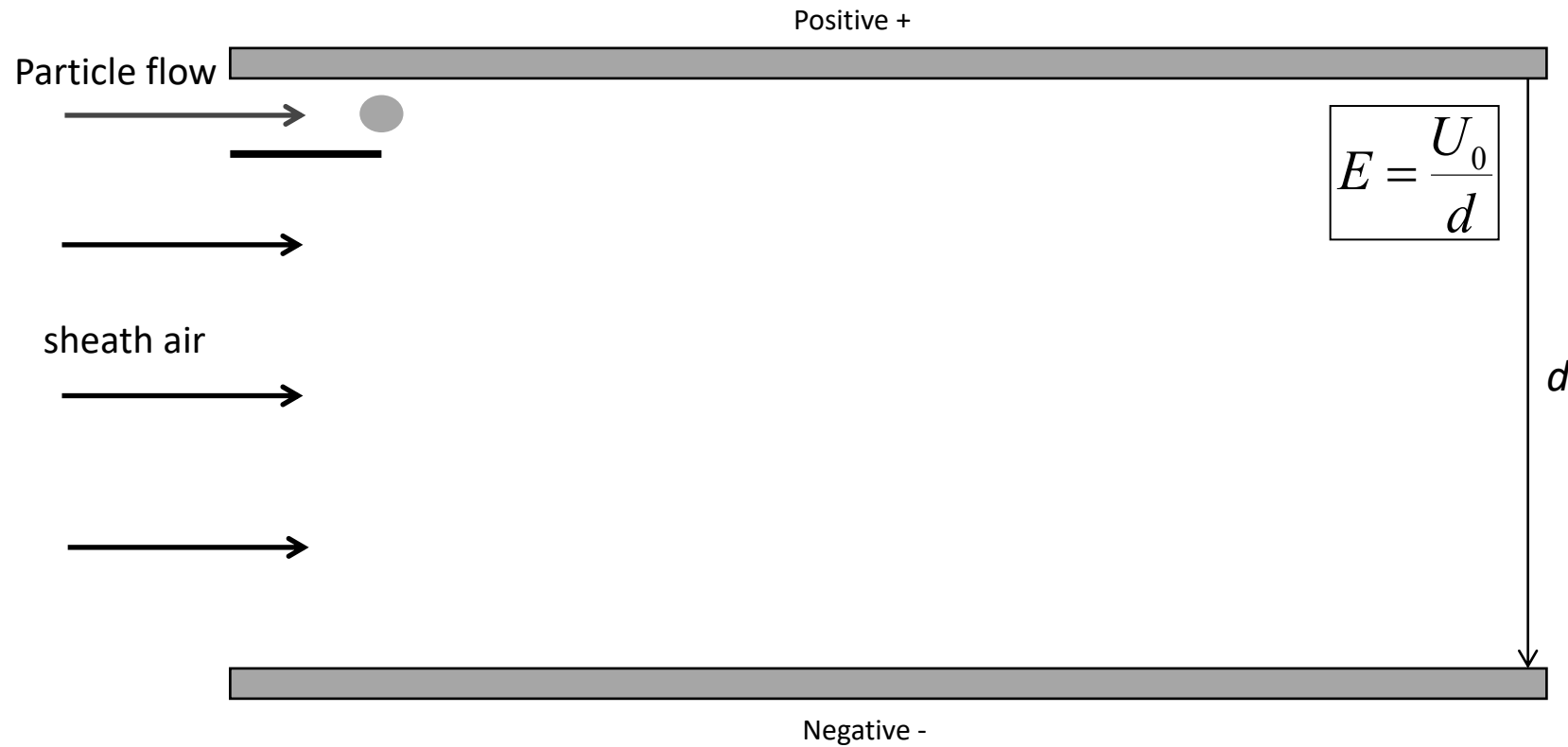
The electrical mobility Z_p of a particle with a certain electric charge is defined to:

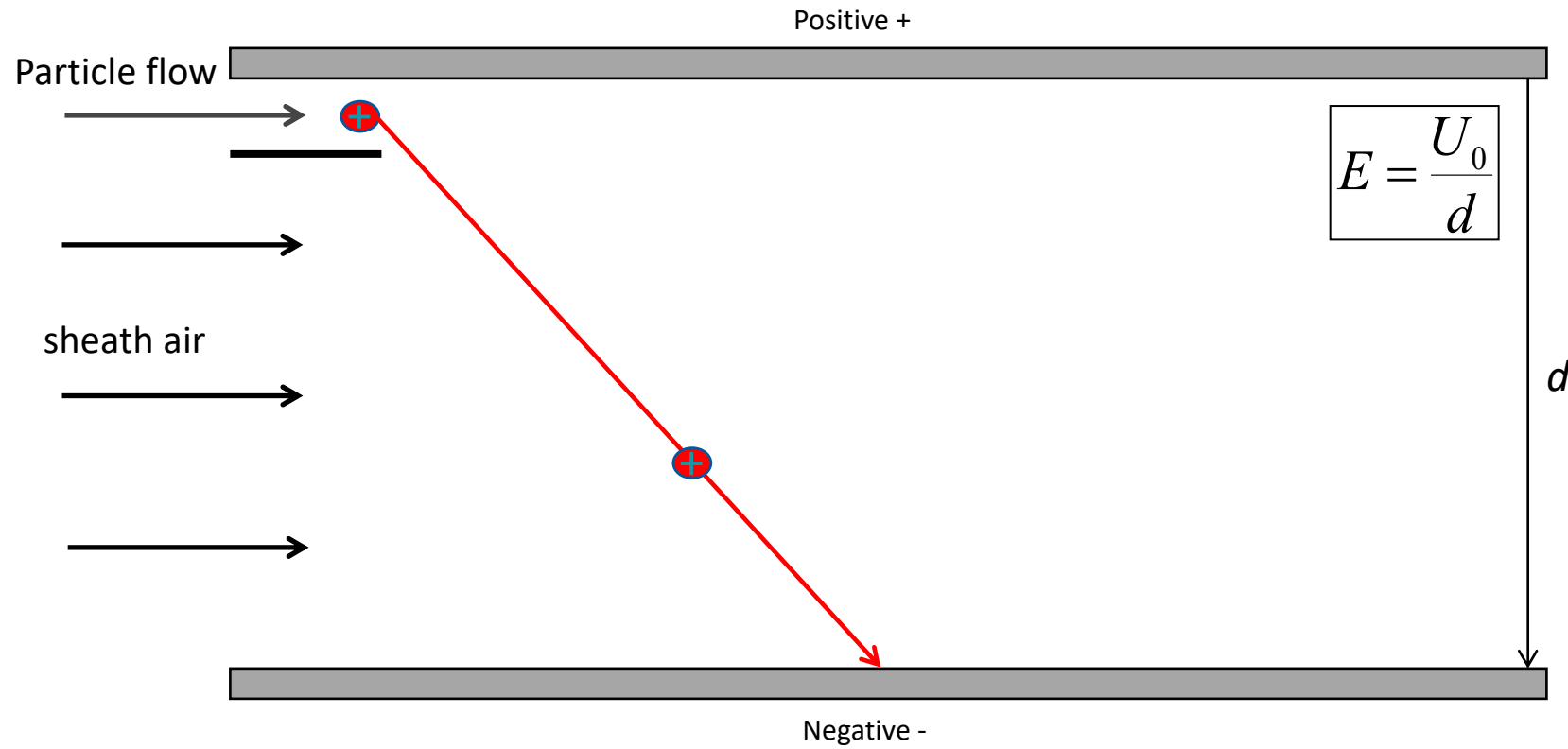
$$Z_p = \frac{\vec{u}_e}{\vec{E}} = n_e \cdot e \cdot \frac{C_C}{3\pi \cdot \eta \cdot D_p}$$

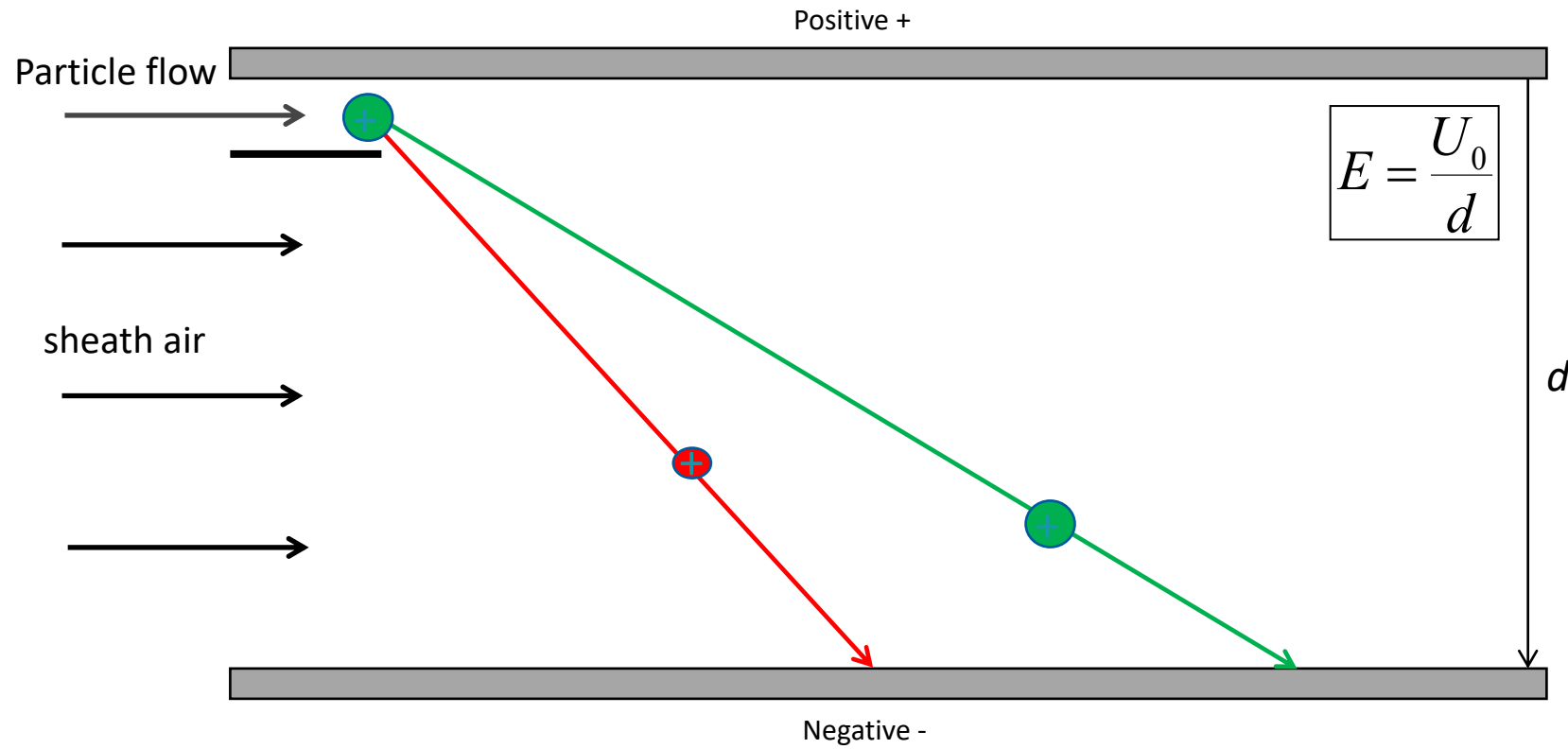
Plate capacitor

$$E = \frac{U_0}{d}$$

d ... distance between the plates







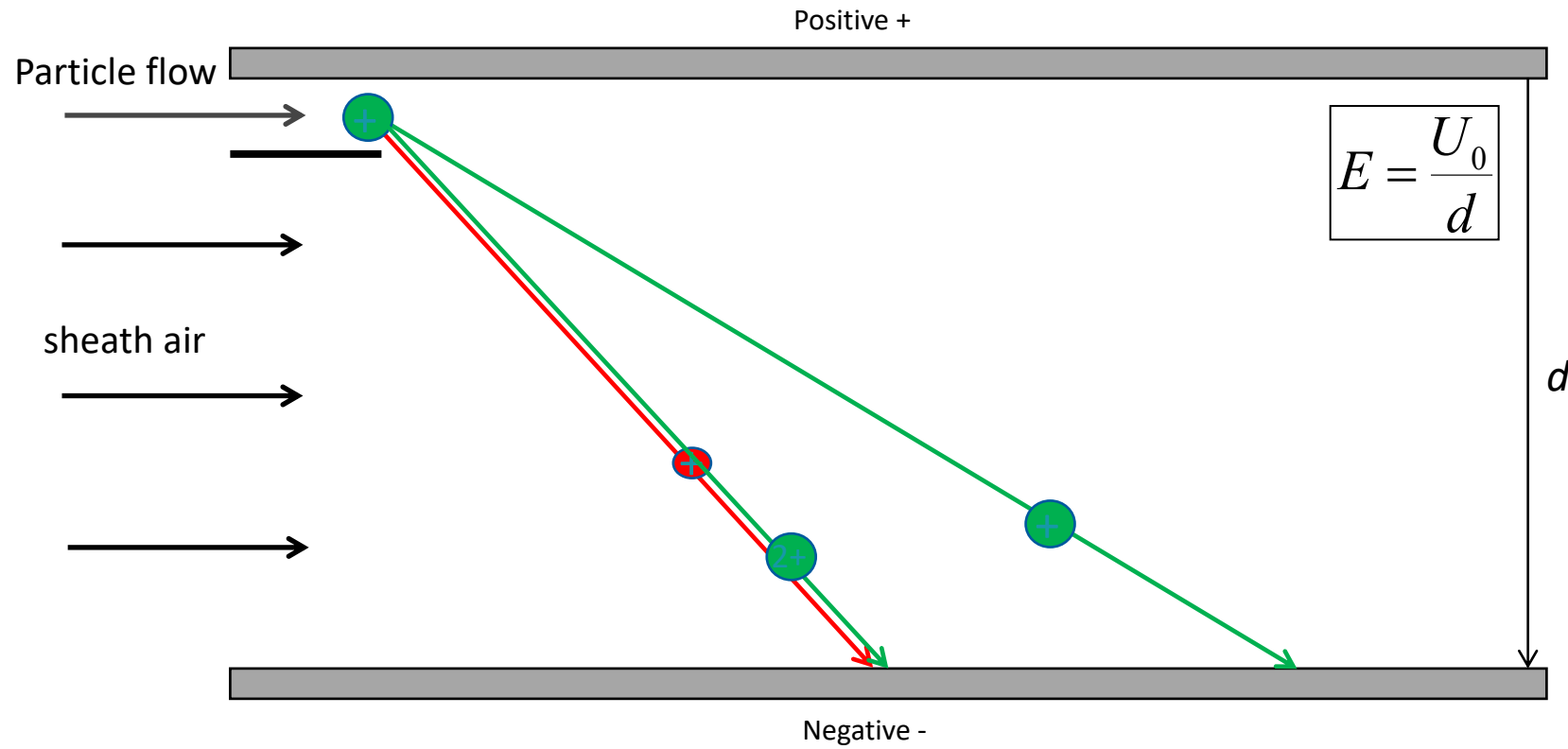
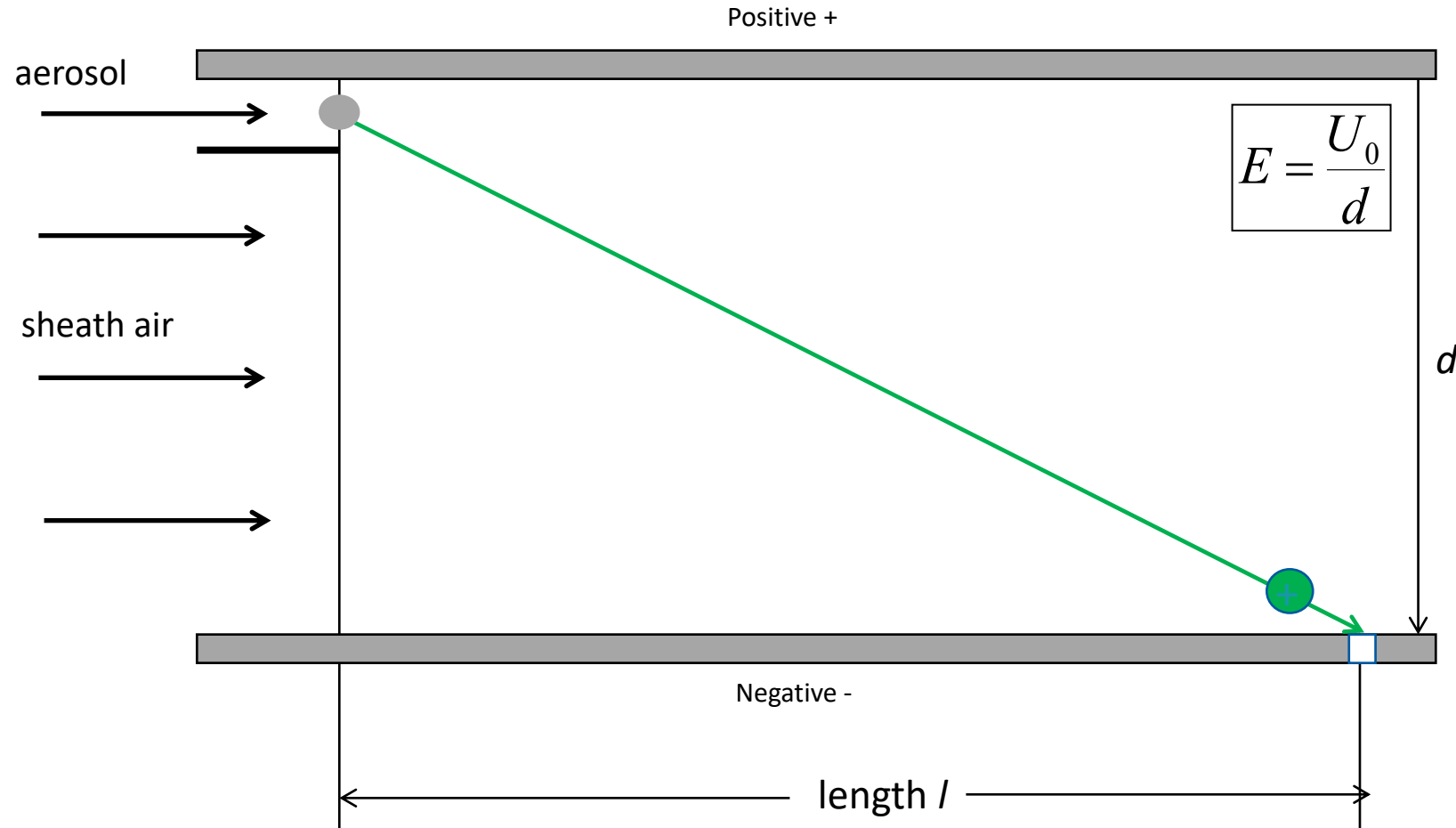


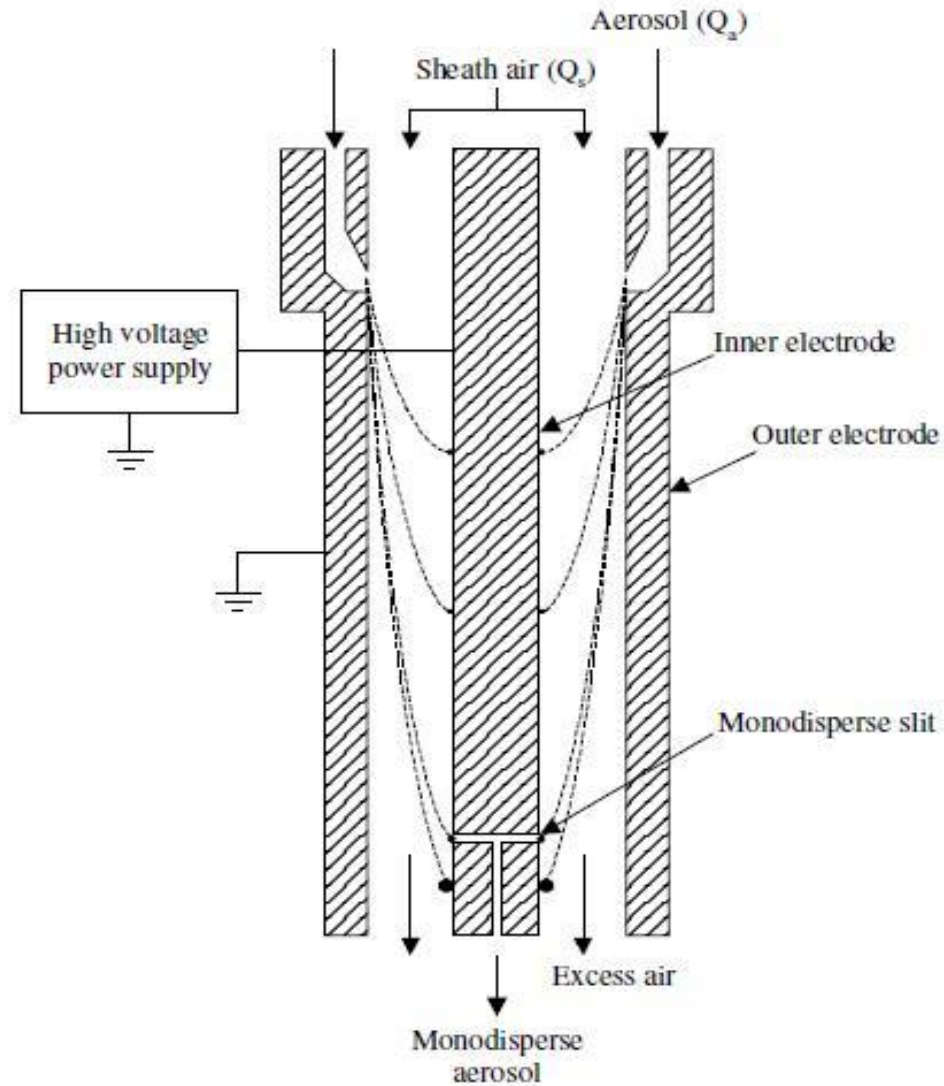
Plate differential mobility analyzer



Cylindrical Differential Mobility Analyzer-

Vienna-Type Differential Mobility Analyzer

$$E = \frac{U_0}{\ln(r_o/r_i) \cdot r}$$



DMA – General Equations

The **voltage** to select the mean electrical particle mobility can be calculated to:

$$\frac{n_e \cdot e \cdot C_C}{3\pi \cdot \eta \cdot \bar{D}_P} = \frac{Q_{Sh} \cdot \ln(r_o/r_i)}{2\pi \cdot U \cdot 1}$$

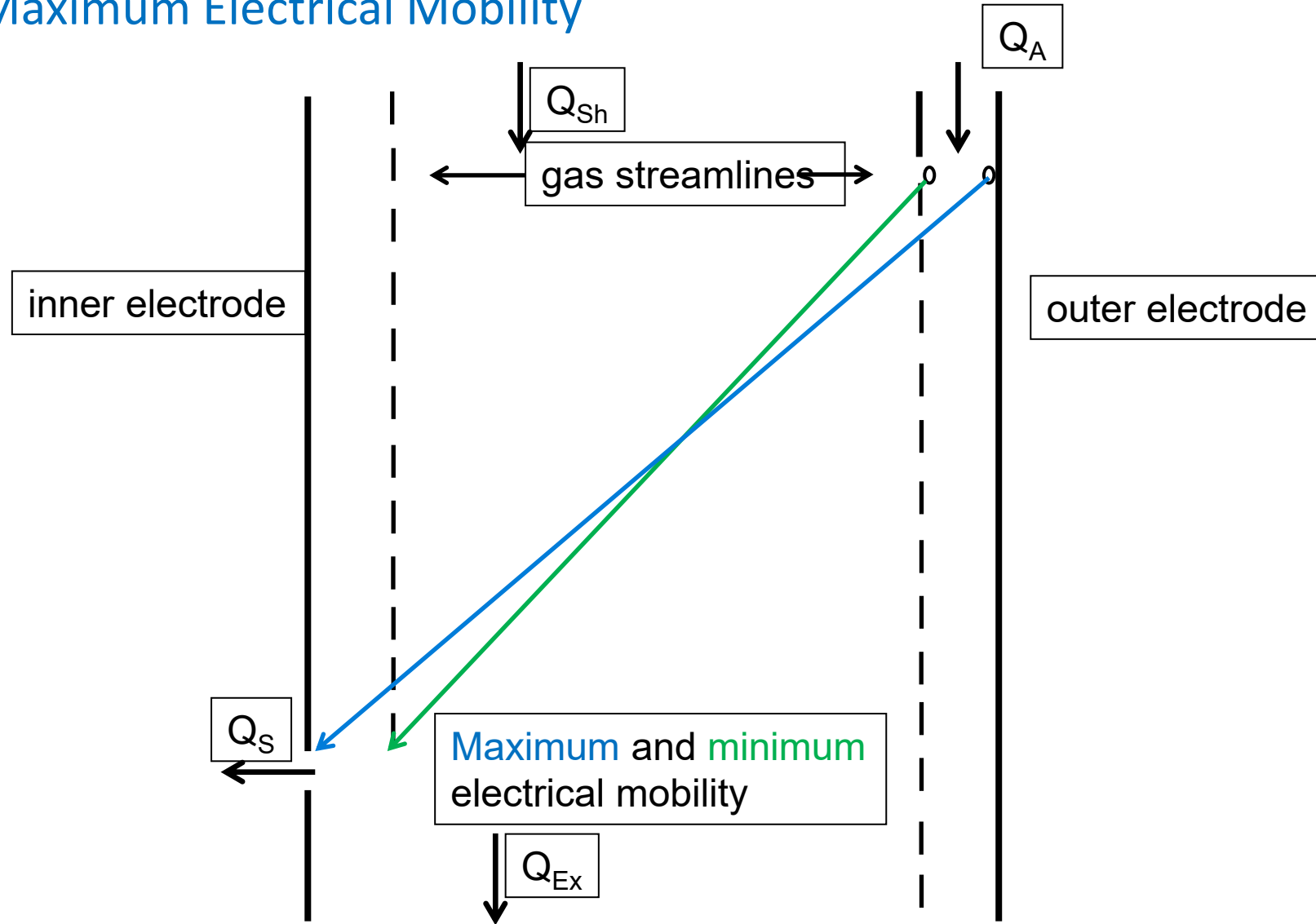
$$\rightarrow U = \frac{3\eta \cdot \bar{D}_P \cdot Q_{Sh} \cdot \ln(r_o/r_i)}{2 \cdot 1 \cdot n \cdot e \cdot C_C(\bar{D}_P)}$$

The **mean particle diameter** can be calculated as follows, but it cannot be analytically solved:

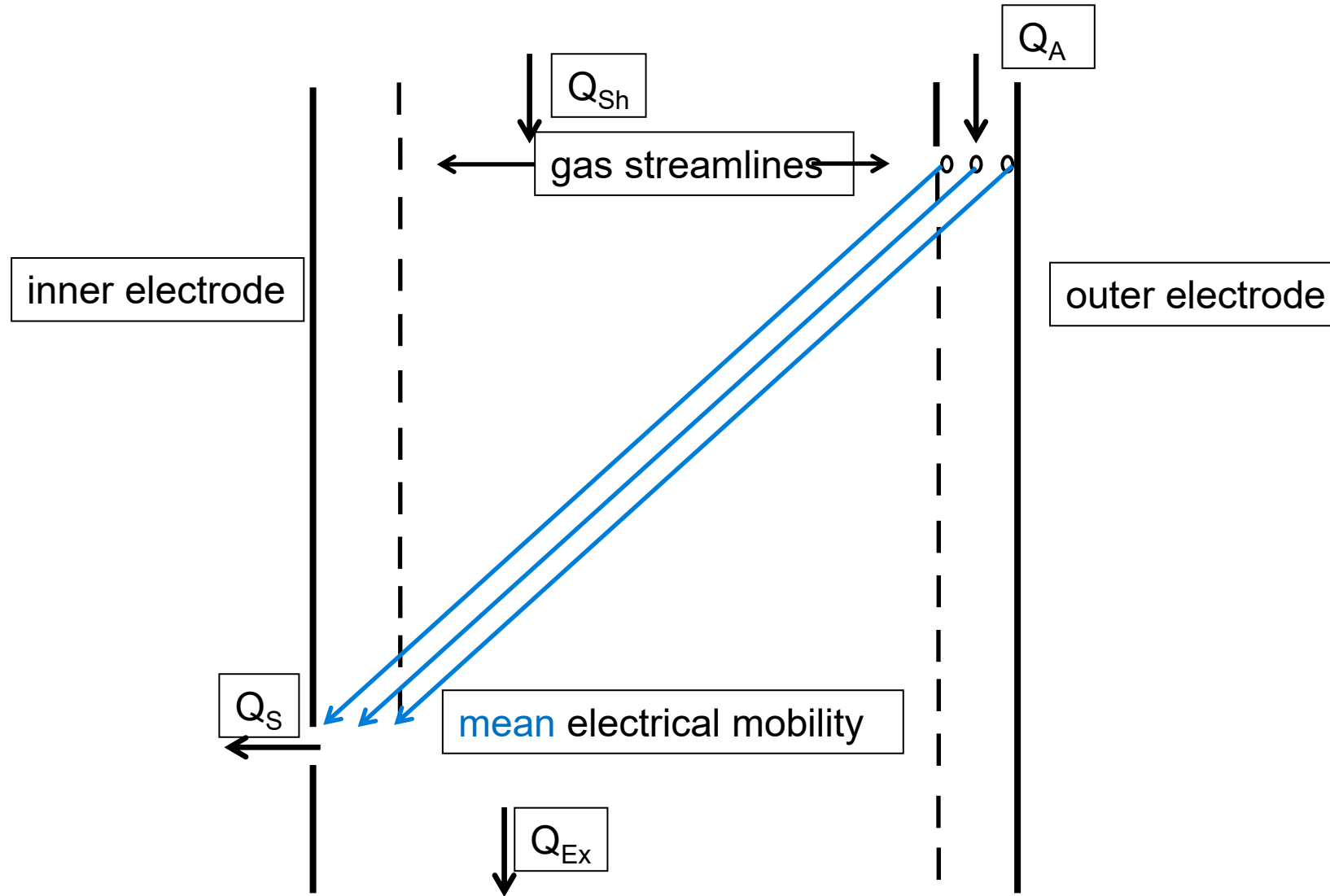
$$\rightarrow \bar{D}_P = \frac{2 \cdot U \cdot 1 \cdot n_e \cdot e \cdot C_C(D_P)}{3\eta \cdot Q_{Sh} \cdot \ln(r_o/r_i)}$$

DMA - Transfer Function

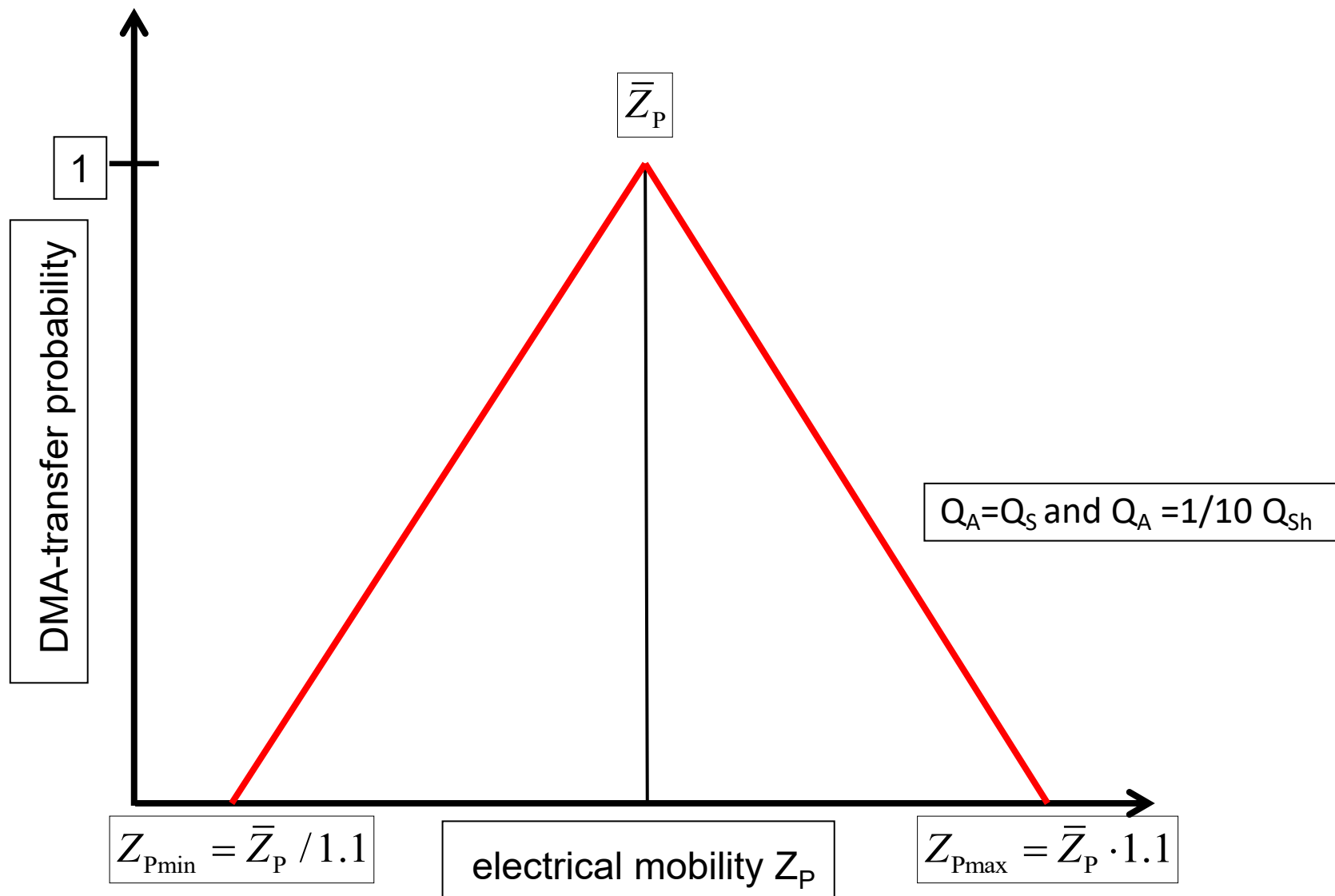
Minimum & Maximum Electrical Mobility



Mean Electrical Mobility



DMA - Transfer Function



DMA - Transfer Function

The flow rate Q_s is taken out of the DMA through a slit at the end of the inner rod, carrying particle with a certain electrical mobility.

The **mean electrical mobility** of these particles can be calculated to:

$$\bar{Z}_P = \frac{(Q - \frac{1}{2}(Q_A + Q_S)) \cdot \ln(r_o/r_i)}{2\pi \cdot U \cdot l}$$

$$\bar{Z}_P = \frac{Q_{Sh} \cdot \ln(r_o/r_i)}{2\pi \cdot U \cdot l}$$

The **ideal width and selectivity** of the electrical mobility bin is described to:

$$\Delta Z_P = \frac{(Q_A + Q_S) \cdot \ln(r_o/r_i)}{2\pi \cdot U \cdot l}$$

$$\frac{\Delta Z_P}{\bar{Z}_P} = \frac{Q_A + Q_S}{Q_{Sh}}$$

$$\frac{\Delta Z_P}{\bar{Z}_P} = \frac{1}{5} \quad Z_P = \bar{Z}_P \pm 0.1 \cdot \bar{Z}_P$$

If $Q_A = Q_S$ and $Q_A = 1/10 Q_{Sh}$