Atmospheric Aerosol Physics, Physical Measurements, and Sampling

Bipolar Charging & Condensation Particle Counters

São Paulo School of Advanced Science on Atmospheric Aerosols:
properties, measurements, modeling, and effects on climate and health

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European Center for Aerosol Calibration

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Particle Charging

General comments

- One of the most important effects in aerosol mechanics is the transport of electrically charged particles in an electric field.
- The electrostatic force can be much greater than e.g. the gravitational force.
- Aerosol particles can be either uncharged, multiply, positively or negatively charged.
- The transport of aerosol particles in an electric field is widely used, mainly in electric particle filters, aerosol collectors, and instrumentation to measure size distributions.

Electric force

- The fundamental equation, which describes the electrostatic force F_{el} between two charges is called Coulomb‘s law.

$$\boxed{F_{\mathrm{el}} = \frac{q_1 \cdot q_2}{4 \cdot \pi \cdot \varepsilon_0 \cdot r^2}}$$

with

ε_0	… permittivity; 8,854.10-12 As/Vm
q_1, q_2	… charges
r	… distance between the charges

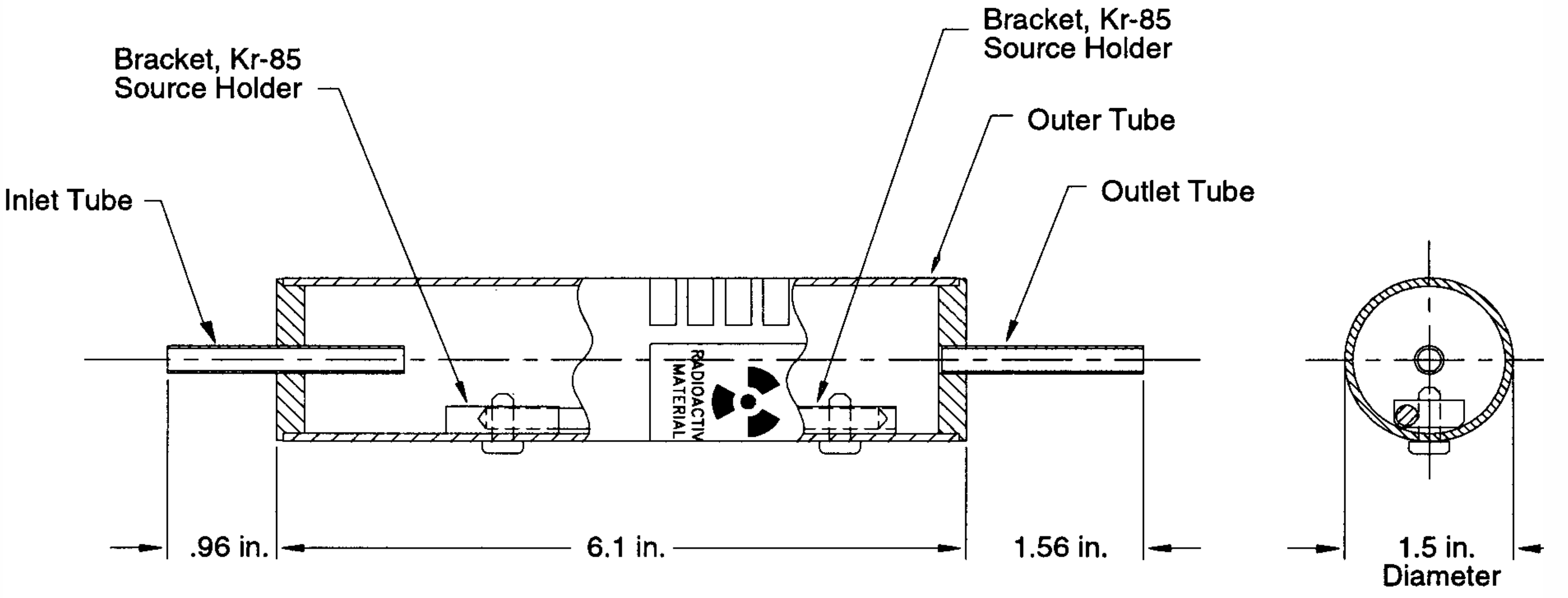
- The electrostatic force can be either repulsive (q_1 und q_2 are both positive or negative) or attractive (q_1 positive und q_2 negative, or vice versa).
- The electrical force of a charge in front of a surface with a different dielectric constant is called image force (decreases with the power of three of the distance).

Bipolar Diffusion Charging

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 due to
    - Diffusion
    - Coulomb forces
    - Image forces

Example: Bipolar Charger TSI 3077A



(Manual: Neutralizer TSI 3077A)

Bipolar charge distribution

- 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:
    - negatively and positively charged particles
    - uncharged, singly and multiple charged particles
- 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).

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

Theory of the Bipolar Charge Distribution

Gunn distribution

- The Gunn 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.

$$F(n)=\frac{\mathrm{e}}{\sqrt{4\pi^{2}\cdot D_{\mathrm{P}}\cdot k\cdot T}}\cdot\exp\left(-\frac{\left(n-\left(\frac{2\pi\cdot\varepsilon_{0}\cdot D_{\mathrm{P}}\cdot k\cdot T}{e^{2}}\right)\ln\frac{Z_{\mathrm{I+}}}{Z_{\mathrm{I-}}}\right)^{2}}{\left(\frac{4\pi\cdot\varepsilon_{0}\cdot D_{\mathrm{P}}\cdot k\cdot T}{\mathrm{e}^{2}}\right)}\right)$$

Fuchs-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 taken into account.
- The Fuchs theory describes the bipolar charge distribution for the entire submicrometer 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.

$$\boxed{F(n) = 10^{\sum_{i=0}^{5} a_i(n)(\log D_\mathrm{P}/\mathrm{nm})^i}}$$

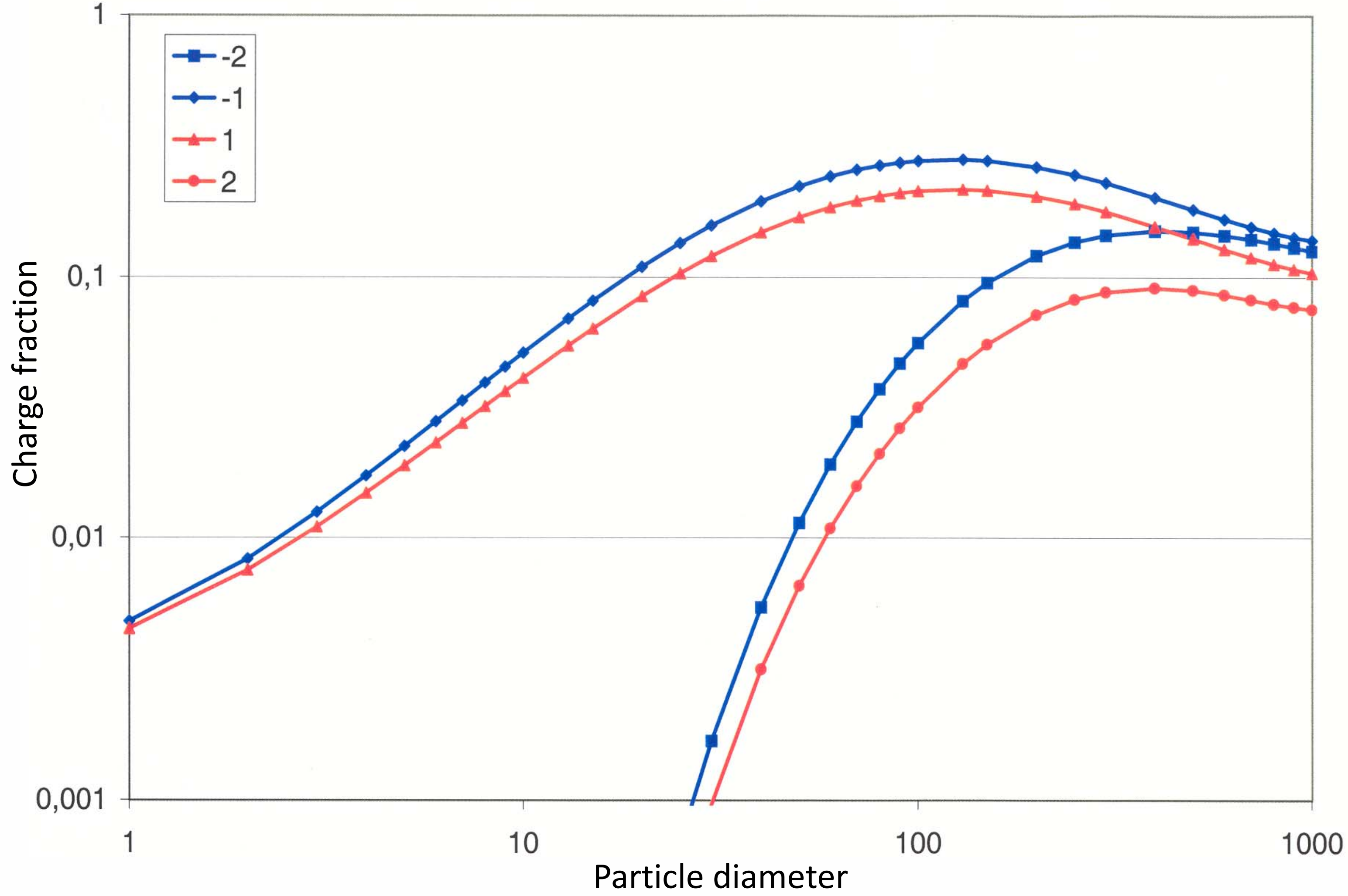
Approximation coefficients

	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

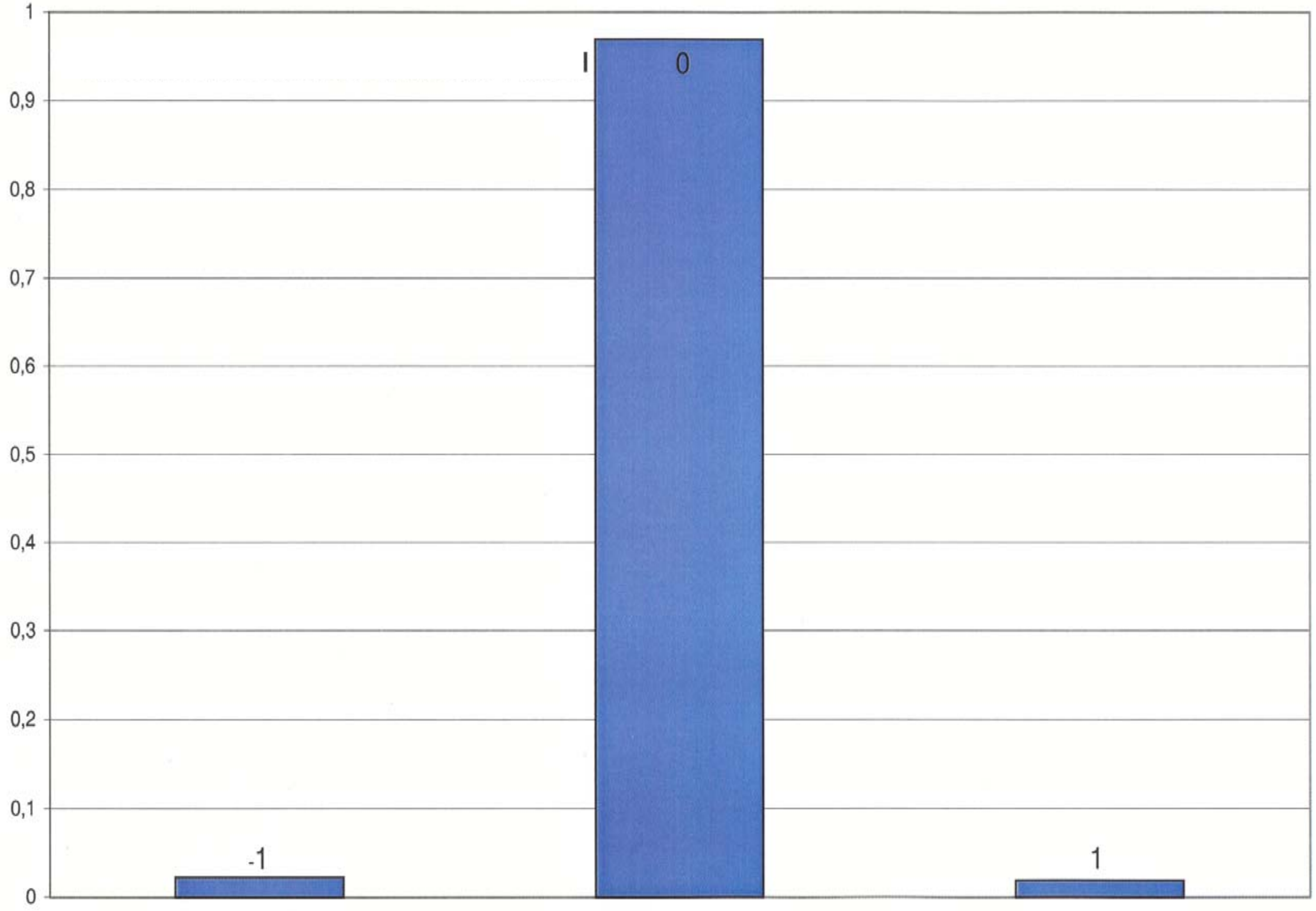
The fractions of multiple charged particles (-2, -1, 0, +1, +2) can be calculated using the approximation formula.

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

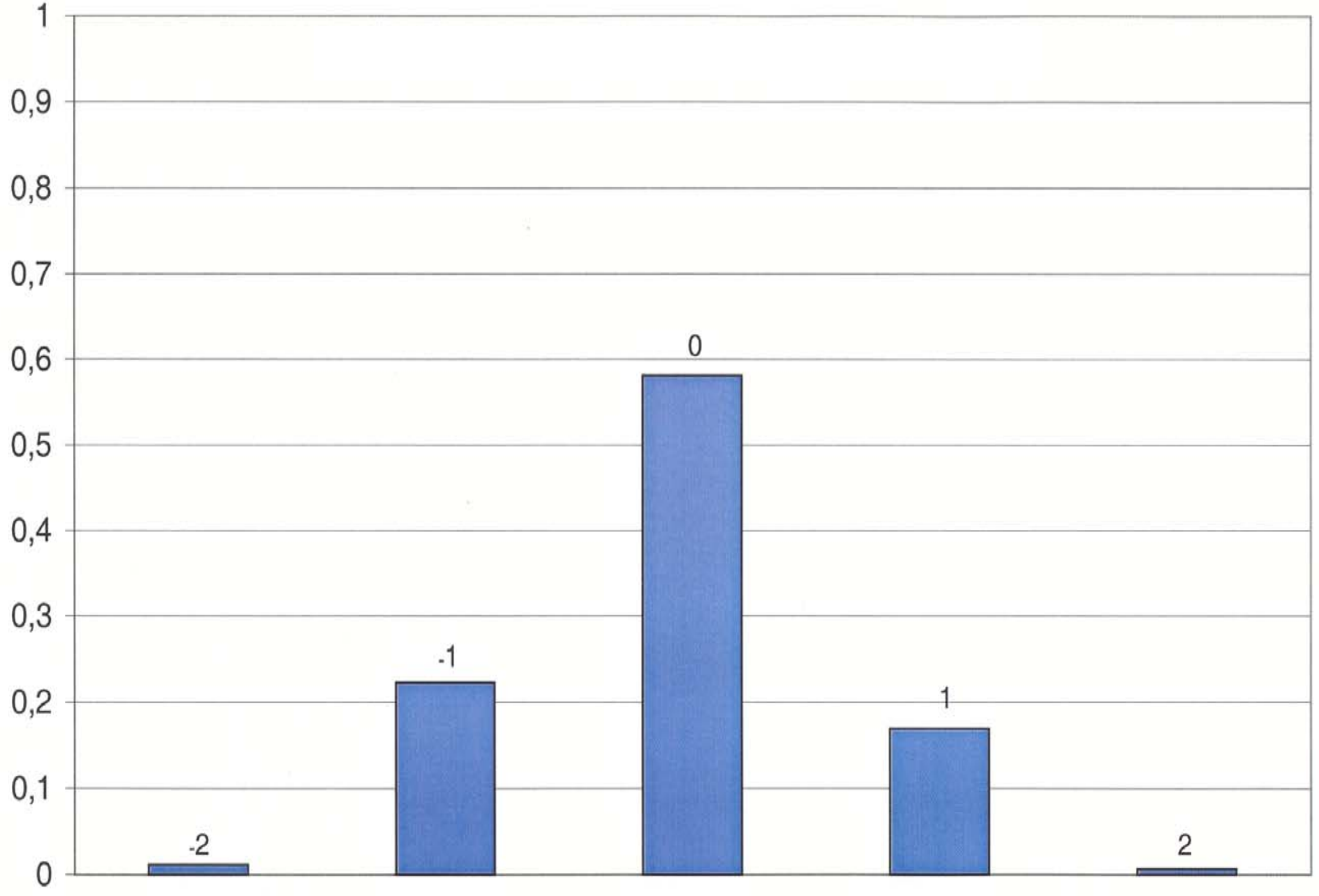
Bipolar charge distribution: singly and doubly charged particles



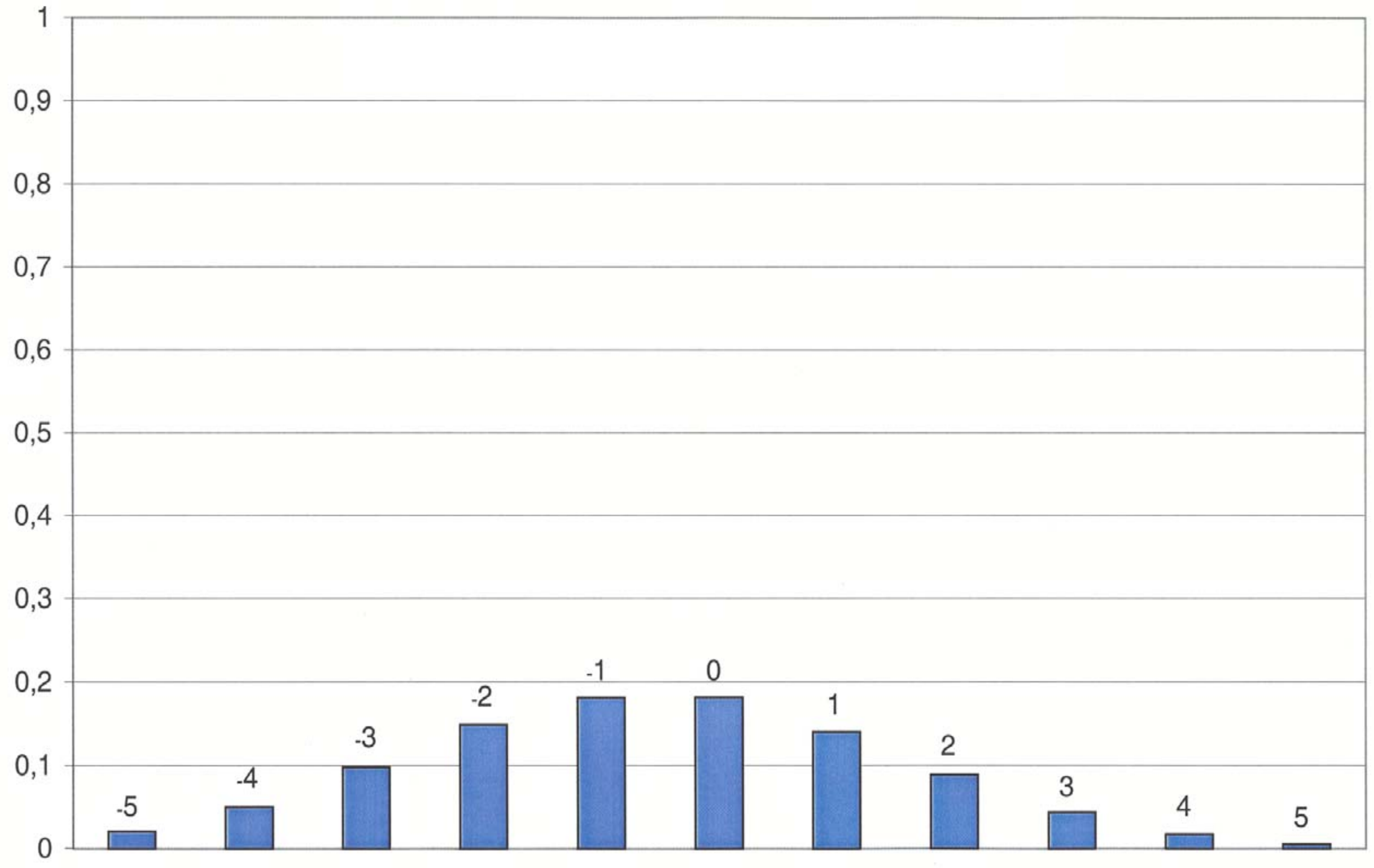
Bipolar charge distribution: 5 nm particles



Bipolar charge distribution: 50 nm particles



Bipolar charge distribution: 500 nm particles



Bipolar charge distribution: submicrometer particles

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

Mean particle charge

An approximation formula can be used to calculate the mean particle charge for particles larger than 100 nm.

$$\boxed{\overline{n} = \frac{D_{\mathrm{P}} \cdot k \cdot T}{2\mathrm{e}^2} \ln\left(1 + \frac{\pi \cdot D_{\mathrm{P}} \cdot c_{\mathrm{I}}^2 \cdot \mathrm{e}^2 \cdot N_{\mathrm{I}} \cdot t}{2k \cdot T}\right)}$$

c_I … mean thermal ion velocity
N_I … ion concentration
t … charging time

Particle Counting

Principle of a CPC

- A Condensation Particle Counter (CPC) and is used to measure the particle number concentration down to few nanometer in particle size.
- The lower detection efficiency is much lower compared to an optical particle size spectrometer.
- The aerosol flow is saturated with a vapor of a working fluid.
- The particle subsequent enlarged to droplets by condensation of a condensable gas. The particles reach a size at which they can be optically detected.
- The number concentration is measured for all particle larger than the lower detection diameter.

The lower detection diameter

- the Kelvin diameter (supersaturation)
- diffusion coefficient of the condensable gas
- the particle material

The lower detection limits are specific for each CPC type.

Following techniques in the past

- microscope (particles collected on a plate)
- picture (cloud chamber)
- extinction
- single particle in a continuous flow
- expansion chamber CPC (extinction)

Modern type of CPCs

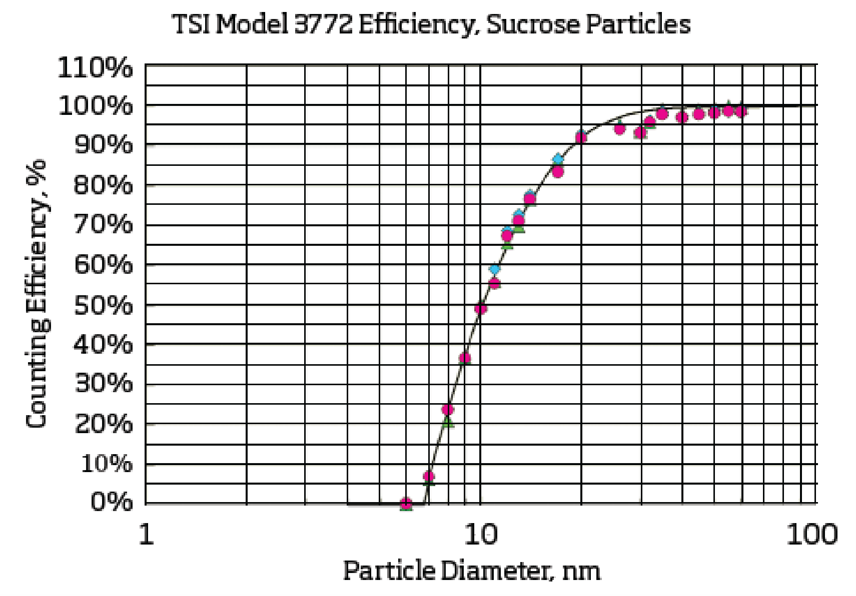
- continuous flow CPC (single particle)

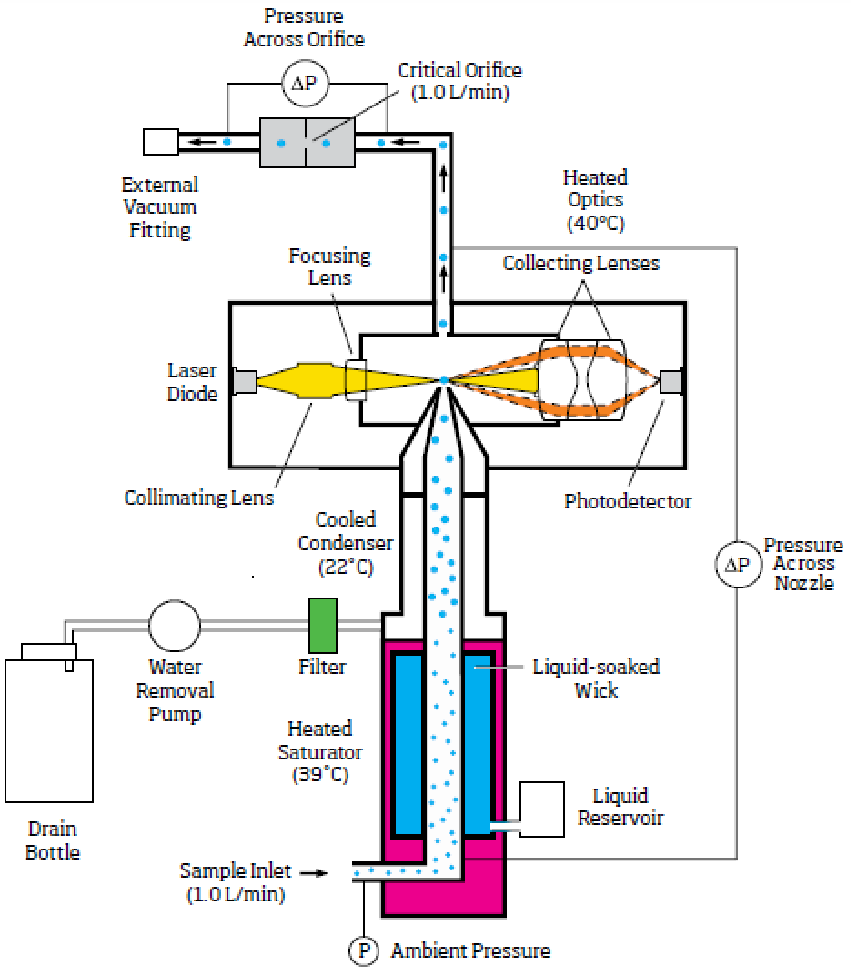
Continuous Flow CPC

Butanol CPC

- The aerosol flow is saturated with butanol in a slightly heated saturator.
- The temperature of the butanol-aerosol mixture is decreased by 17-27°C in the condenser of the CPC.
- The butanol becomes supersaturated and condenses onto the particles.
- The particles grow to droplets of several µm in diameter.
- The droplet flow is focused in a nozzle and introduced into a counting optic.
- The droplets pass a laser beam, and each single particle creates a light pulse.
- Pulses with an amplitude above a certain threshold are counted.
- The particle number concentration can be calculated by knowing the aerosol flow rate.

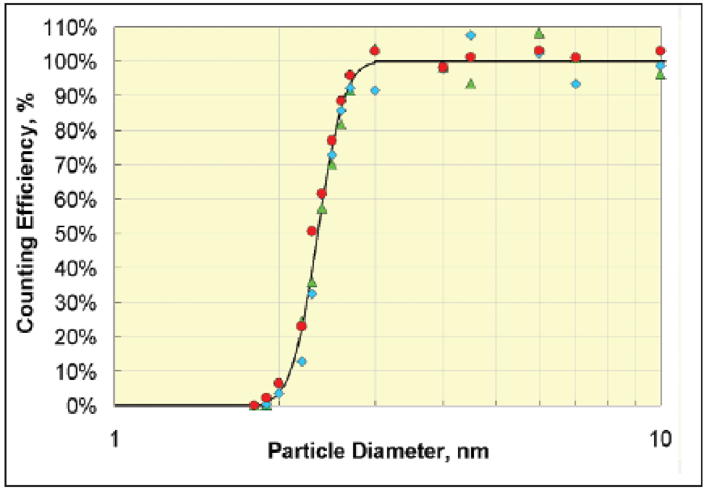
CPC TSI model 3772/3750

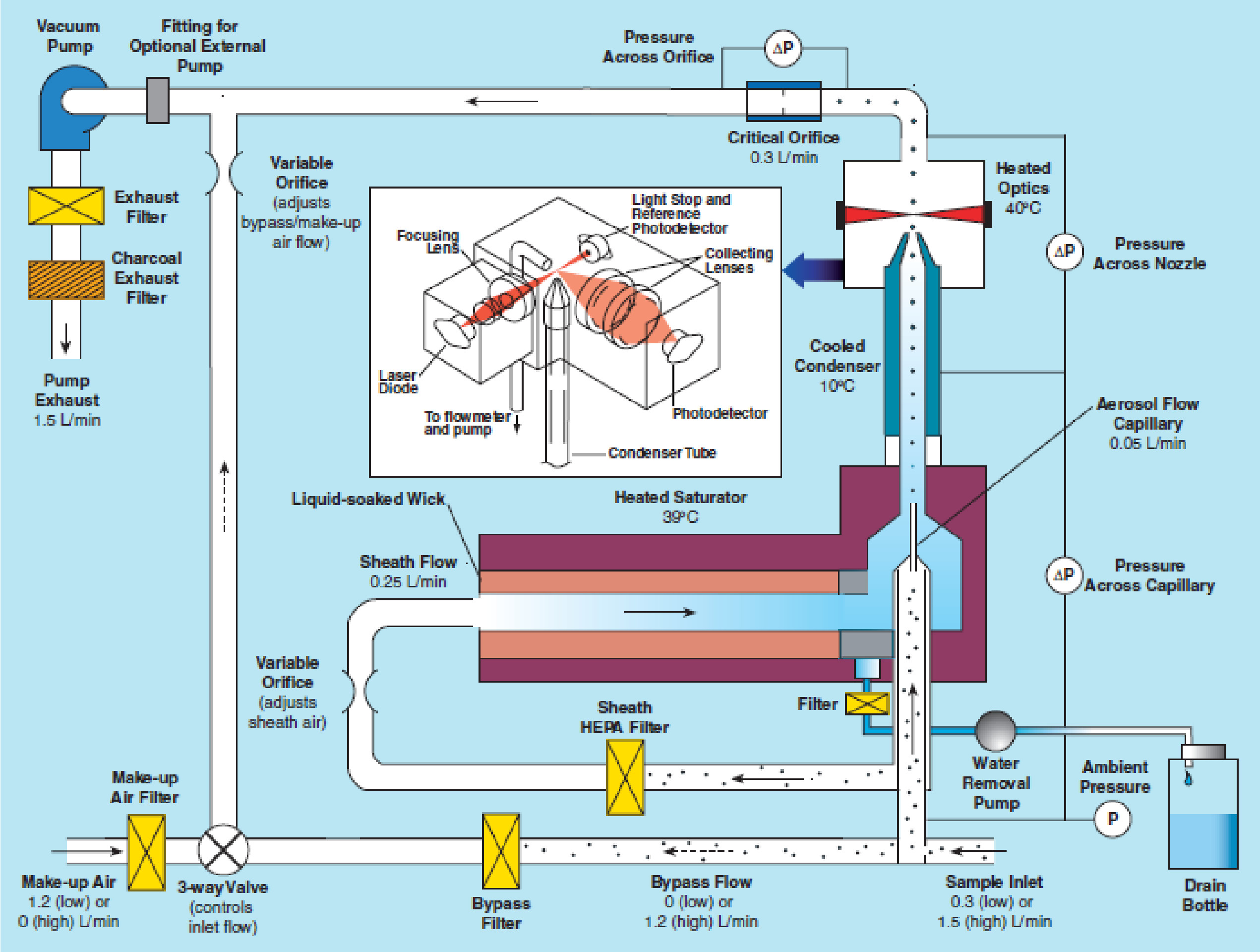




CPC TSI model 3776/3756

TSI Model 3776 Efficiency, Sucrose Particles



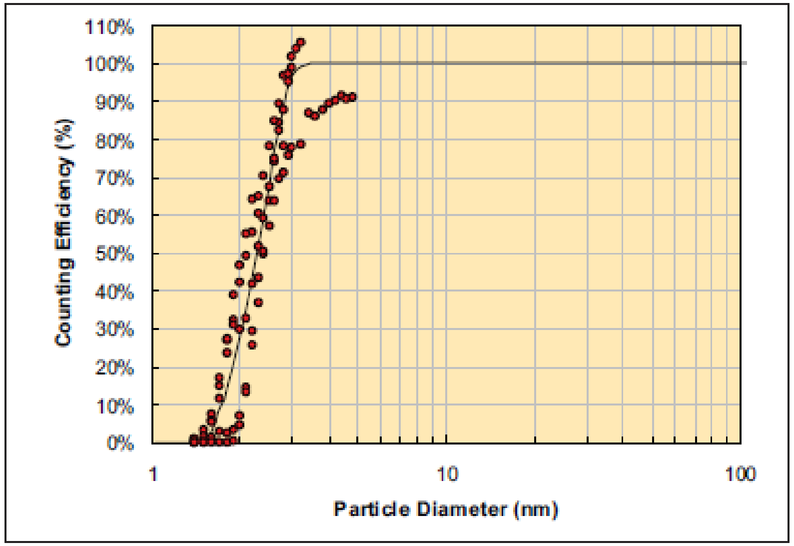


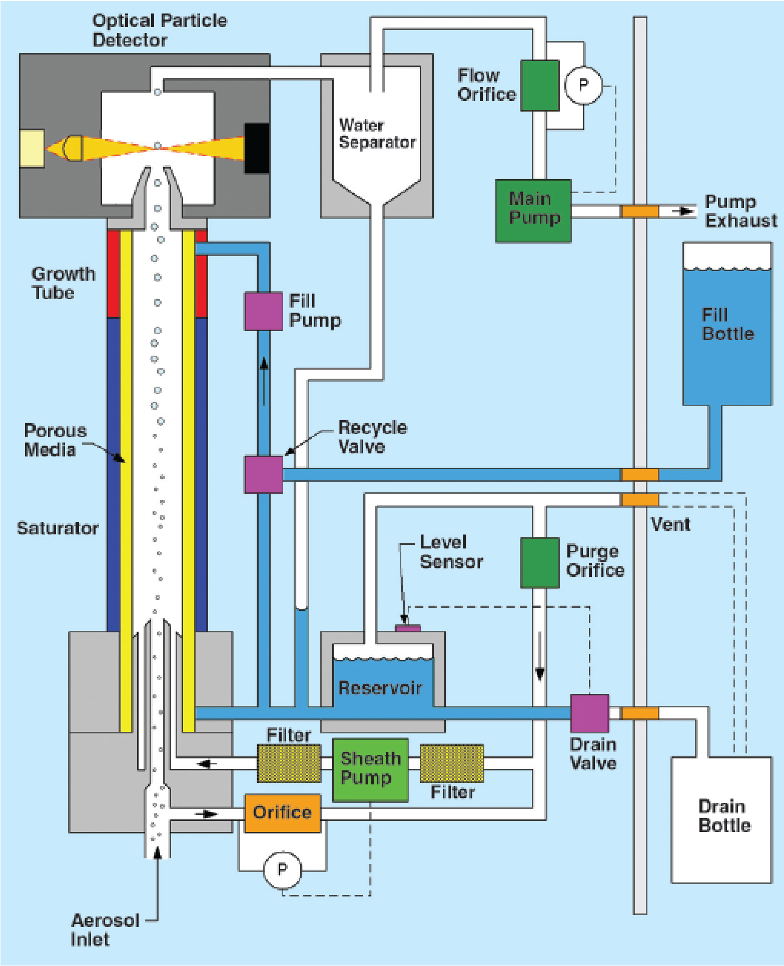
Water CPC

- Instead of alcohol, water is used for the measurement of sub-micrometer aerosol particles.
- The aerosol flow is saturated with water vapor and temperature equilibrated in a cooled saturator.
- Then the flow passes through a condenser with heated walls, which contain water. This produces an elevated vapor pressure.
- Evaporated water vapor diffuses faster to the center of the aerosol flow than the heat from the walls and thus supersaturates it.
- The particles act as condensation nuclei when they are larger than the activation size and grow quickly to droplets of a detectable size.
- The droplet flow is focused in a nozzle and introduced into a counting optic.
- The droplets pass a laser beam, and each single particle creates a light pulse.
- Pulses with an amplitude above a certain threshold are counted.
- The particle number concentration can be calculated by knowing the aerosol flow rate.

TSI CPC model TSI 3786/3788

TSI Model 3786 Efficiency





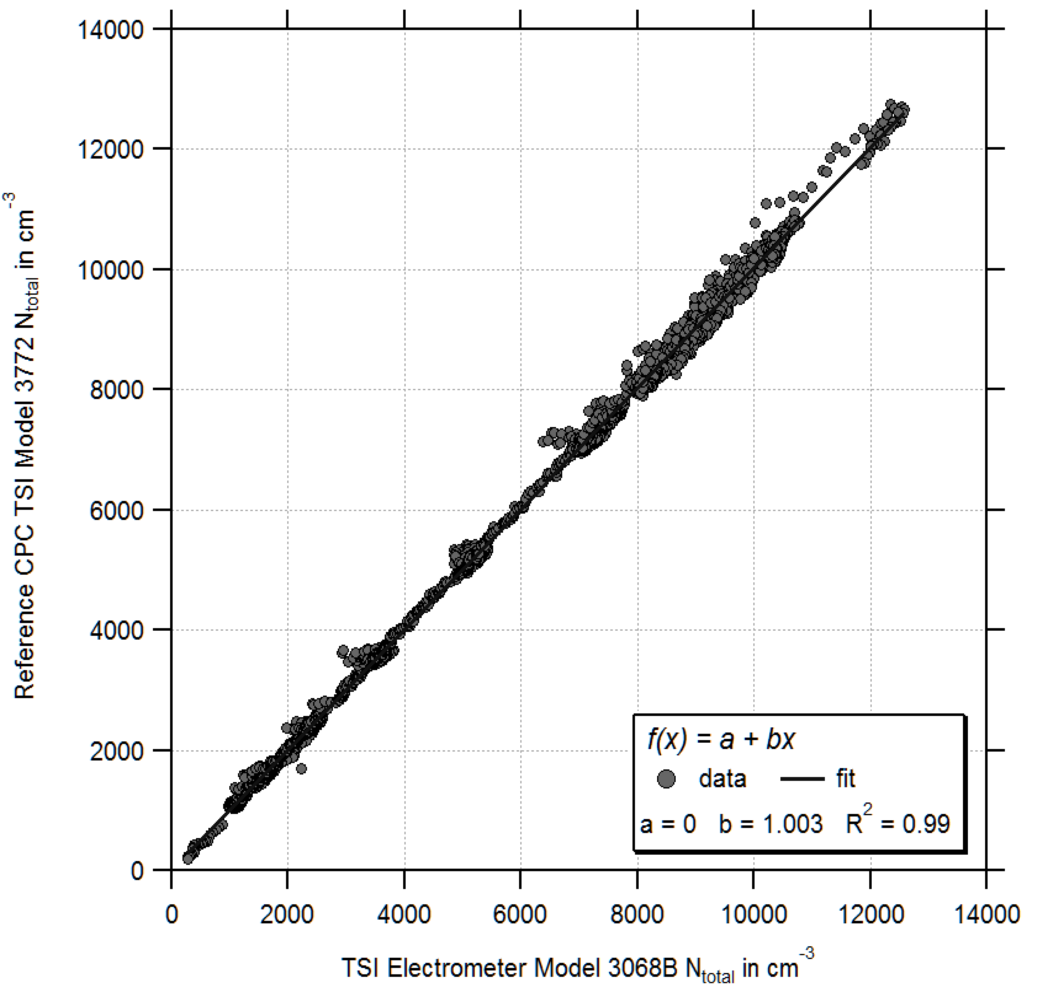
CPC - Traceability & Calibration

Wiedensohler, A. et al. (2018). Mobility Particle Size Spectrometers: Calibration Procedures and Measurement Uncertainties. Aerosol Science & Technology **52**(2), 146–164.

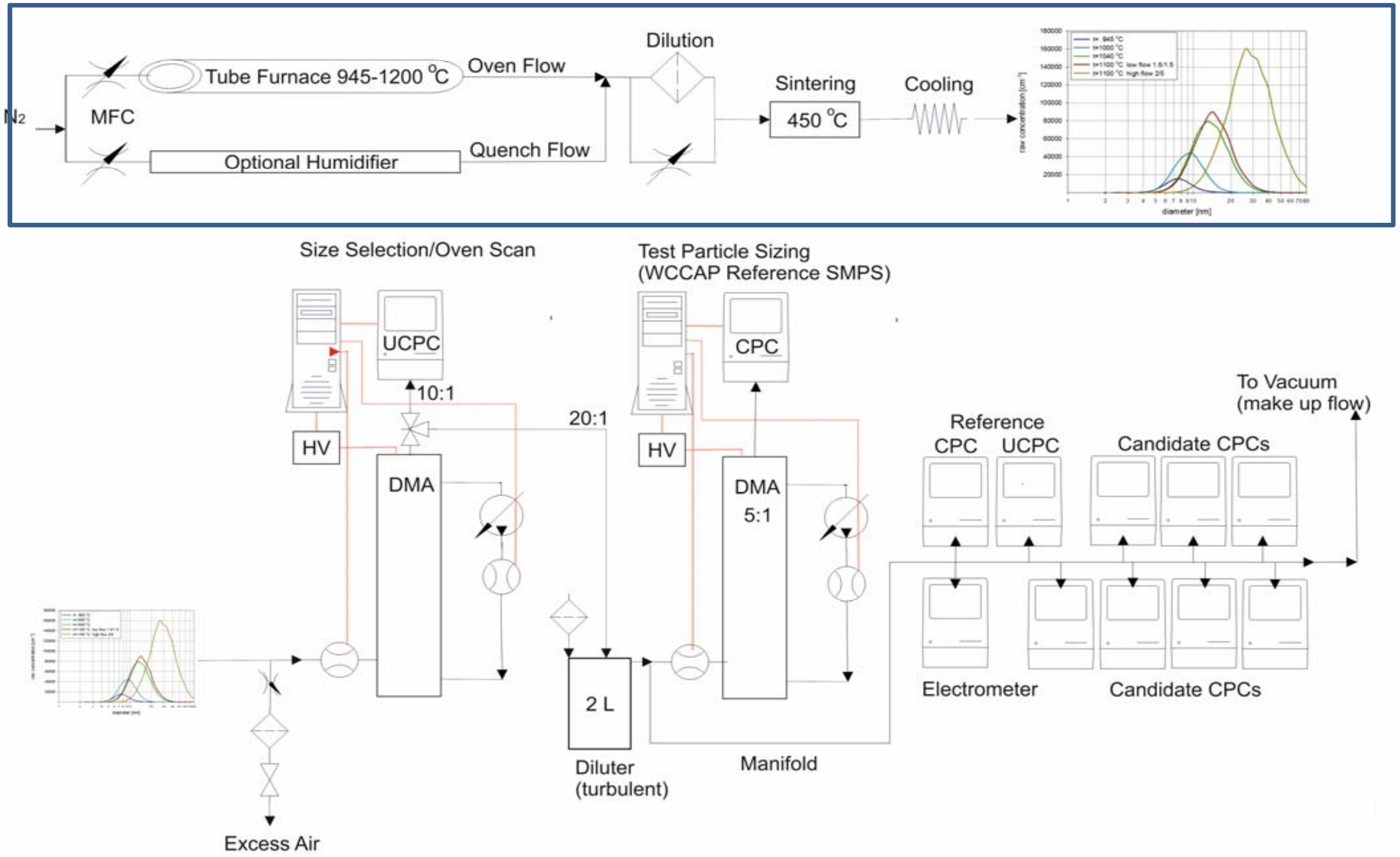
Particle Number Concentration

- There is no direct standard for a particle number concentration!
- The reference concentration is determined from an independent aerosol electrometer measurement
- Following calibration chain is applied:
  - Calibration of an aerosol electrometer against a femto-A source (at a metrology institute such as NIST, NPL, PTB)
  - Calibration of reference condensation particle counter
  - Calibration of individual instruments

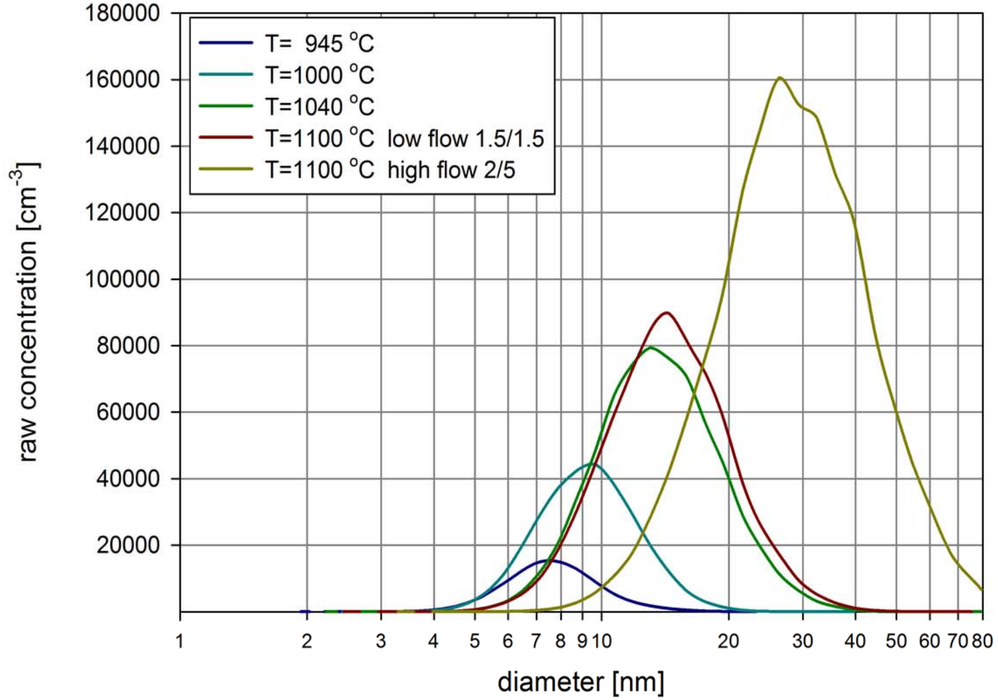
Reference Electrometer - CPC

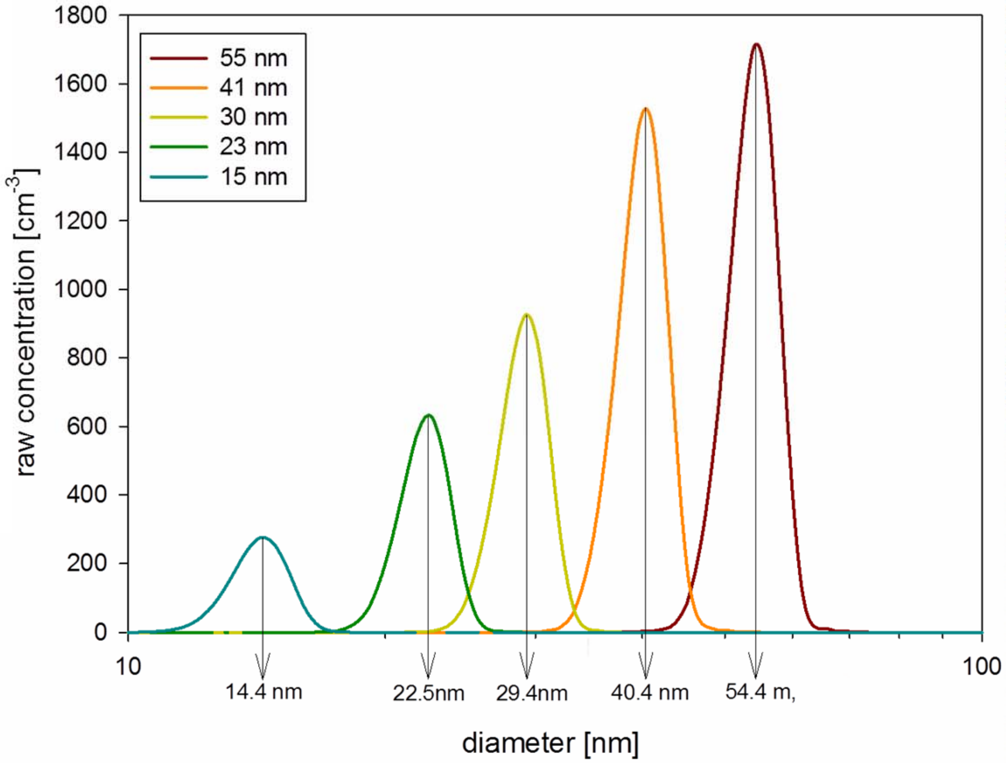


CPC - Calibration Set-Up



Tube Furnace Generator & Particle Selection





Calibration: CPC TSI models 3772, 3776