

FUNDAMENTALS OF CONDENSATION PARTICLE COUNTERS (CPC) AND SCANNING MOBILITY PARTICLE SIZER™ (SMPS™) SPECTROMETERS

APPLICATION NOTE CPC-003 (US)

Introduction

When using aerosol measurement instruments, it is important to have a basic understanding of the fundamental physics and calculations behind their operation. Condensation Particle Counters (CPCs) are used to measure total number concentration of an aerosol, while Scanning Mobility Particle Sizer (SMPS) spectrometers are used to measure size distributions of aerosols.

CPC Working Principles

CPCs function by counting individual particles and outputting a particulate concentration. Particles are grown by creating vapor from a working fluid (usually butanol, isopropyl alcohol, or water) which condenses onto the particles so they grow in size and can be optically counted. See Figure 1.

The lower limit of particle detection is usually considered to be the size at which the CPC can detect 50% of the particles, referred to as the d_{50} of the CPC. An example CPC efficiency curve for a 3772 CPC is shown in Figure 2.

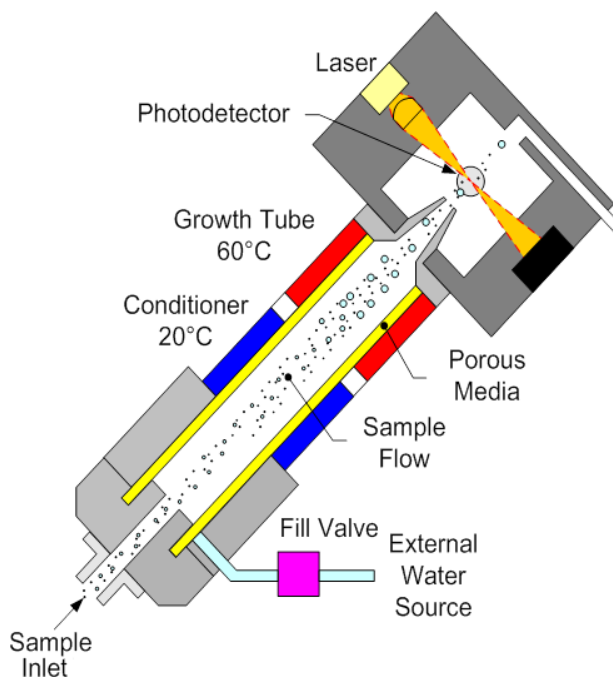


Figure 1: Basic water-based CPC flow schematic

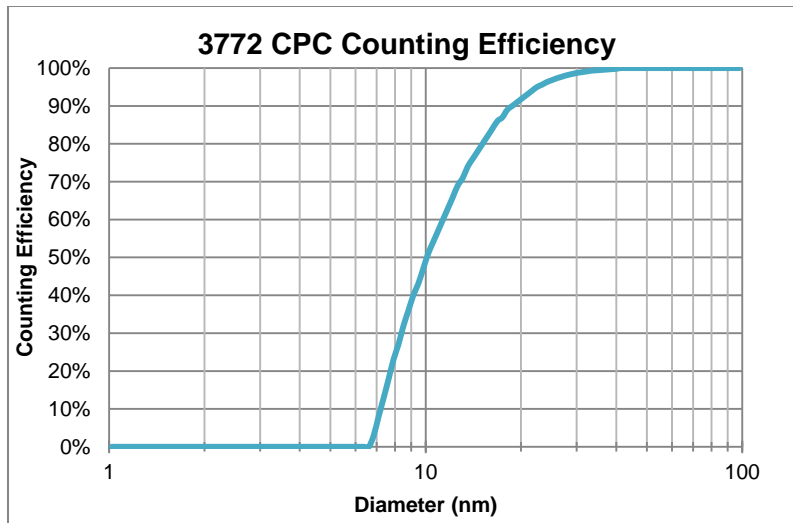


Figure 2: Counting efficiency curve of 3772 CPC

Total particle counts from the CPC for a certain sample time (usually 1s) are then divided by the product of sample time and flow rate to determine the particle concentration as shown below:

$$CPC \text{ Concentration} \left[\frac{\text{particles}}{\text{cm}^3} \right] = \frac{CPC \text{ Counts} [\text{particles}]}{Sample \text{ Time} [s] * CPC \text{ Flow rate} \left[\frac{\text{Liters}}{s} \right] * 1000 \left[\frac{\text{cm}^3}{\text{Liter}} \right]}$$

Equation 1

It is important to remember that the particle concentration measured by the CPC is the total number concentration of all particles that the CPC can detect. For example, using the curve shown in Figure 2, 50% of 10 nm particles will be detected by a 3772 CPC. Because the CPC alone has no ability to differentiate between particles of different sizes, the total number concentration cannot be corrected using the CPC efficiency curve.

SMPS Spectrometer Principles

An SMPS spectrometer system consists of an electrostatic classifier to sort particles based on their electrical mobility and a CPC to count the sorted particles. An electrostatic classifier uses a bipolar neutralizer to apply a standard equilibrium charge distribution to the aerosol and a differential mobility analyzer (DMA) to select the aerosol based on electrical mobility. The fundamental inverse relationship between the electrical mobility and particle size allows the SMPS system to generate an aerosol size distribution using the following principles:

Differential Mobility Analyzer (DMA)

DMAs are the tools used to separate aerosols based on electrical mobility. Electrical mobility is a particle property that depends on both the size and the charge state of the particle. A diagram of a DMA is shown in Figure 3.

A DMA column consists of a center rod and an outer grounded tube. A high voltage is applied to the center rod. The difference in voltage between the rod and the tube generates an electric field. The aerosol sample is drawn into the space between the center rod and the outer tube and drawn toward the bottom of the column. As the aerosol sample flows from the top to the bottom of the column, the charged particles are either forced to the outer tube or drawn to the inner rod by the electric field depending on their polarity. The uncharged particles pass through the column, unaffected by the electric field.

Particles with a higher electrical mobility are drawn towards the inner rod at a faster rate than those with a lower electrical mobility. As seen in Figure 3, since the particles flow toward the bottom of the column at a constant rate, the electrical mobility of a particle together with the strength of the electric field determine where the particle will impact the center rod. For a given voltage, particles with a high electrical mobility will impact the rod sooner than those with a low electrical mobility. There is a slit near the base of the rod. Particles that would normally impact the rod in this location pass through the slit and exit the DMA; therefore, for a given voltage, only particles with a certain electrical mobility will pass through the slit. Thus, a DMA is used to classify polydisperse aerosol particles based on electrical mobility since the voltage on the rod can be directly related to the electrical mobility of the particles exiting the DMA. In an SMPS system, a classifier scans across a voltage range while a CPC counts the classified particles, generating a size distribution.

Since electrical mobility depends on particle size and particle charge, **for a classifier to accurately sort particles based on size, the charge of the particles must be controlled.** A polydisperse aerosol can have any charge distribution. In the SMPS spectrometer system, the charge distribution of the polydisperse aerosol is standardized using an aerosol neutralizer (either radioactive or soft x-ray) prior to size classification the DMA.

Aerosol Neutralization

An aerosol neutralizer standardizes the sample aerosol by subjecting the sample aerosol to ionic atmosphere, leaving the aerosol with a stationary state charge distribution. Historically, a Boltzmann equilibrium distribution has been used to approximate the charge state of a neutralized aerosol; however, this approximation assumes equilibrium and neglects image forces and the increase in ion concentration at the surface of the particle and is only applicable in the particle diameter range of 0.2 to 2 μm .

The Fuchs limiting sphere charge distribution model (1963) accounts for these deviations from equilibrium and is widely accepted; however, it must be solved numerically due to its complexity. Wiedensohler (1988) developed an approximation for the stationary state charge distribution of an aerosol in a bipolar ionic atmosphere, accurate below 1 micrometer. The Boltzmann distribution, Fuchs distribution, and Wiedensohler approximation for charge probability as a function of size are shown in Figure 4 through Figure 6 for 0-2 charges.

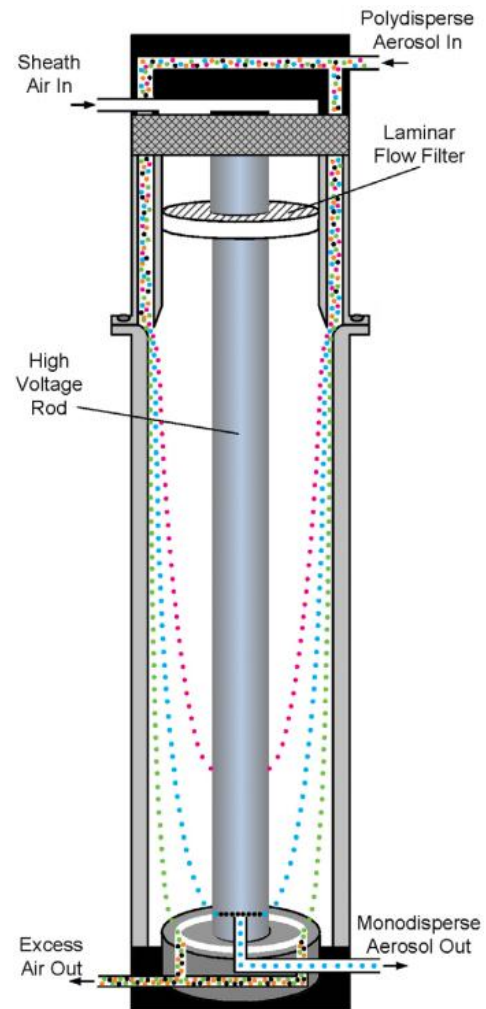


Figure 3: Differential mobility analyzer schematic

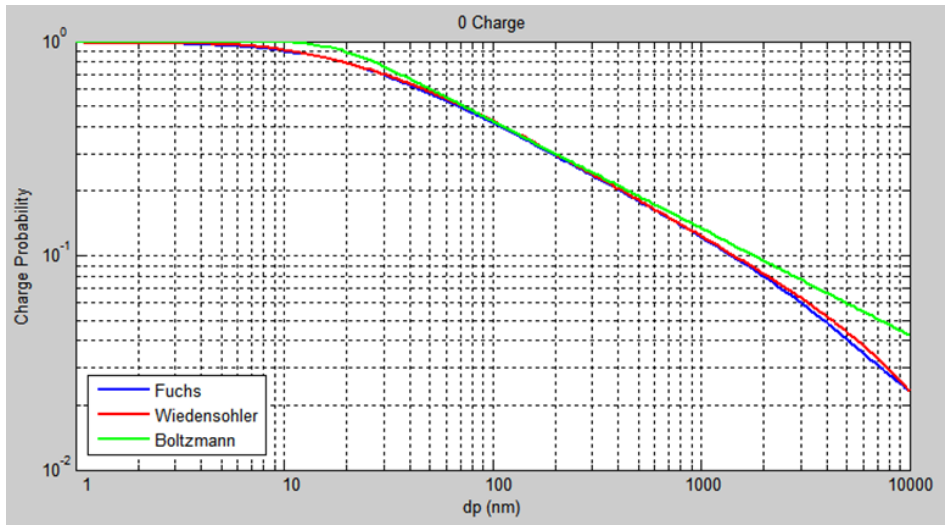


Figure 4: Equilibrium 0 charge probability as a function of particle diameter

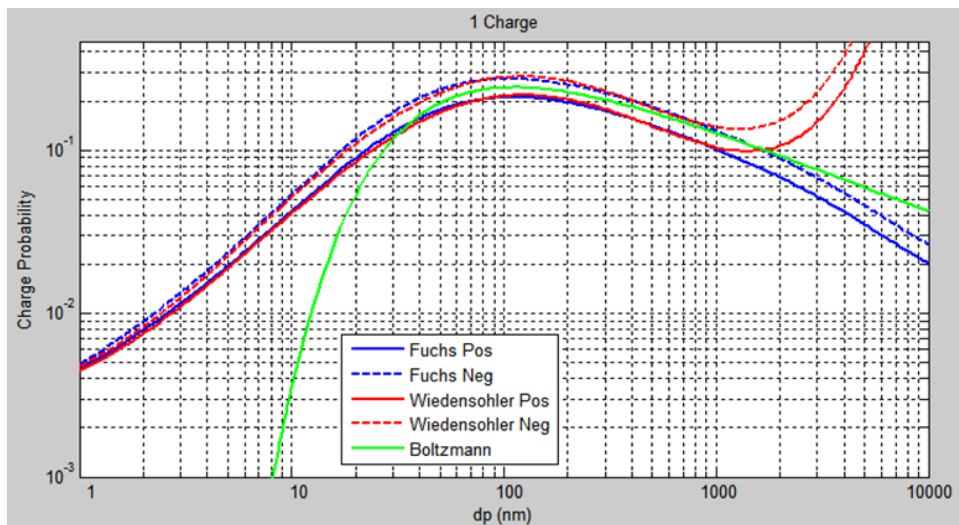


Figure 5: Equilibrium 1 charge probability as a function of particle diameter

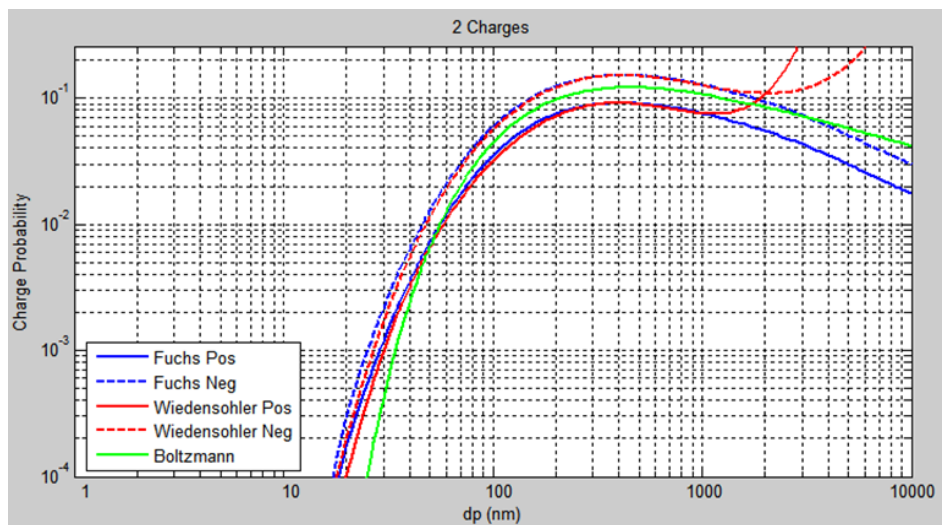


Figure 6: Equilibrium 2 charge probability as a function of particle diameter

As seen in Figure 4, the majority of particles in the submicron range have no charge. Figure 5 shows that in the range of particle sizes measured by the SMPS spectrometer, 1-20% of particles will have 1 charge and that above 200 nm, roughly 10% of particles are doubly charged.

SMPS Spectrometer Calculations

Aerosol Instrument Manager® software uses the DMA voltage, the CPC concentration, the CPC efficiency curve, and the Wiedensohler equations to calculate the aerosol size distribution:

- An aerosol neutralizer is used to apply a stationary-state charge distribution on the particles.
- The electrostatic classifier is used to select particles of a single electrical mobility
- The CPC counts the selected particles
- The voltage on the DMA determines the electrical mobility of the particles that pass through the DMA at a given time
- The Wiedensohler approximation is used to determine the fraction of particles at a certain size that are singly charged
- The CPC efficiency curve is used to determine the fraction of particles of that size that are detectable by the CPC

This charge efficiency fraction and CPC detectable fraction are combined with the fraction of particles measured by the CPC to calculate the total concentration of particles of each size. These size-resolved particle concentrations are combined to generate an aerosol size distribution.

Complicating Factors

There are several factors that affect the SMPS spectrometer concentrations that need to be considered.

The first factor is that due to the Fuchs stationary-state charge distribution, only a small fraction (approximately 1-20%) of particles are singly charged and make it through the DMA. Thus, any variability in particle count or charging can be amplified depending on the size of the particle. ***This is especially important at small particle sizes where only a small percentage of the particles are charged and at very low concentrations where there is a higher uncertainty in counting.***

$\sigma = \frac{1}{\sqrt{C}} \times 100\%$ demonstrates the dependence of counting uncertainty on size, where σ is the relative counting uncertainty and C is the particle count (not concentration). Thus, at lower counts, the uncertainty is higher.

$$\sigma = \frac{1}{\sqrt{C}} \times 100\% \quad \text{Equation 2}$$

When comparing total concentration as measured by a CPC to the total concentration as measured by an SMPS spectrometer, concentrations must only be compared over the detectable size range of the CPC. When measuring very small particles near the d_{50} of the CPC, the CPC may not count all of the particles in this range; the SMPS spectrometer will compensate for the CPC efficiency curve because it is able to resolve particle size.

Other factors that may or may not be relevant depending on particle size are diffusion loss, multiple charges on the particles, and the shape of the particles.

Very small particles may be lost due to diffusion to the walls of the tubing in the sample system, the tubing in the classifier, the DMA, the tubing between the classifier and the CPC and prior to the CPC detector. The *Diffusion loss correction* option in Aerosol Instrument Manager Software takes into account the flow rate and dimensions of the aerosol transfer path in the classifier and CPC and corrects the data based on the number of particles that are theoretically lost due to diffusion in the system (see application note SMPS-001).

As seen in Figure 4 through Figure 6, especially for larger particles, a significant fraction of particles may carry multiple charges. Aerosol Instrument Manager software can take these probabilities into account and make a correction for multiply charged particles.

Aerosol Instrument Manager software assumes all of the particles measured are spherical. However, some aerosols, such as soot, are composed of chain aggregates made up of smaller particles. To correct for the variation in electromobility in chain aggregates compared to spherical particles, the aggregate mobility analysis tool within Aerosol Instrument Manager software can be used (see application note SMPS-002). This is especially important when calculating the surface area, volume and mass of the particles. For many particles, the assumption that the particles are spheres is either valid or is a close approximation to the shape of the particle. For chain aggregates, such as soot, this assumption is clearly not valid and the aggregate mobility analysis tool can result in an improved calculation of these parameters.

Summary

An SMPS system and a CPC have two separate purposes. A CPC is designed to measure total particle number concentration, while an SMPS spectrometer is used to measure a quantitative size distribution of a polydisperse aerosol. Because of the differences in principles between the operation of an SMPS spectrometer and a CPC, the total particle concentration calculated using an SMPS spectrometer differs slightly from the total particle concentration measured by a CPC, especially at low concentrations.

Key References

- ❖ N. A. Fuchs, On the Stationary Charge Distribution on Aerosol Particles in a Bipolar Ionic Atmosphere, *Geophys. Pure Appl.* **1963**, 56, 185-193
- ❖ Wiedensohler, An Approximation of the Bipolar Charge Distribution for Particles in the Submicron Size Range, *J. Aerosol. Sci.* **1988**, 19, 387-389
- ❖ [SMPS Spectrometer Bibliography](#)
- ❖ [Aerosol Statistics Lognormal Distributions and \$dN/d\log D_p\$](#) (Application note PR-001)
- ❖ [Scanning Mobility Particle Sizer \(SMPS\) Spectrometer Diffusion Loss Algorithm](#) (Application note SMPS-001)
- ❖ [Scanning Mobility Particle Sizer \(SMPS\) Spectrometer Nanoparticle Aggregate Mobility Analysis Software Module](#) (Application note SMPS-002)
- ❖ More information can be found at www.tsi.com.



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