ATMOSPHERIC ULTRAFINE PARTICLE MEASUREMENTS

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Pasi Aalto
Abstract

This thesis presents details of the construction and calibration of instruments used for atmospheric ultrafine particle measurements. The measurement range of the Differential Mobility Particle Sizer (DMPS) has been extended down to three nanometers and more reliable systems have been constructed for long-term measurements. A completely new instrument for small particle measurements, the Pulse Height Analysis Ultrafine Condensation Particle Counter (PHAUCPC) has been constructed, calibrated and tested in the field. The PHAUCPC has been used together with the DMPS to study the solubility of ultrafine particles in butanol. By studying the particle solubility information about the ultrafine particle chemical composition has been derived. A Cloud Condensation Nucleus counter (CCNC) has been constructed, tested and used in the field. By using the estimated particle soluble fractions from the CCN counter and the Tandem Differential Mobility Analyzer (TDMA) data these two instruments have been compared.

The instruments constructed have been used during measurement campaigns in the Arctic during IAOE-91 and AOE-96, the Finnish Antarctic measurement station ABOA, the subarctic station of Värriö in Lapland, the boreal forest in Hyytiälä, Finland, Helsinki and other cities in Finland, the coastal site in Mace Head, Ireland, the German site in Melpitz, Mediterranean sites in Athens and Marseilles and a marine site on Tenerife, Spain. The essential features of the size distributions like the modal behavior and evolution are described. These instruments have revealed new information on new particle production and particle growth in the atmosphere.
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List of publications

This thesis consists of an introductory review part, followed by six research articles.

I. A. Wiedensohler, P. Aalto, D.S. Covert, J. Heintzenberg and P.H. McMurry, Intercomparison of Four Methods to Determine Size Distributions of Low-Concentration (∼100 cm³), Ultrafine Aerosols (3 nm<D_p<10 nm) with Illustrative Data from Arctic, *Aerosol Science and Technology* 21, 95-109, 1994.


**Acronyms**

A In linear model the matrix that contains the model of the instrument

ABOA – Finnish Antarctic research station

ACE-1 – Southern Hemisphere Aerosol Characterization Experiment

ACE-2 – North Atlantic Regional Aerosol Characterization Experiment

AOE-96 – Arctic Ocean Expedition, 1996

b In linear model the measured coefficients

BIOFOR Biogenic aerosol formation in the boreal forest

CCN Cloud Condensation Nuclei

CCNC Cloud Condensation Nuclei Counter

CPC Condensation Particle Counter

d Diameter (tube)

D Particle diffusion coefficient

DMA Differential mobility analyzer

DMPS Differential Mobility Particle Sizer

D_p Particle diameter

e In linear model the error

EAA Electrical Aerosol Analyzer

EAS Electrical Aerosol Spectrometer

ELPI Electrical Low Pressure Impactor

EMS Electrical Mobility Spectrometer

GAW Global Atmospheric Watch

IAOE-91 International Arctic Ocean Expedition, 1991

L Length (tube)

n_2(Z_i) Mobility distribution

N_1 Particle concentration
PARFORCE New Particle Formation and Fate in the Coastal Environment

PHAUCPC Pulse Height Analysis Ultrafine Condensation Particle Counter

PM Particle mass

PM$_{10}$ Particle mass of particles less than 10 µm in diameter

PM$_{2.5}$ Particle mass of particles less than 2.5 µm in diameter

$q$ In linear model the $\chi^2$ -value

$Q$, $Q_s$ and $Q_a$ Volumetric flowrate, DMA sheath flow rate and DMA aerosol flow rate

Re Reynolds number

RH Relative humidity

$s$ In linear model the errors for the measured coefficients

Sc Schmidt number

Sh Sherwood number

SMPS Scanning Mobility Particle Sizer

TDMA Tandem Differential Mobility Analyzer

TSI TSI Incorporated

$v$ Flow velocity

$v_{\text{diff}}$ Deposition velocity

$x$ In linear model the unknown coefficients

$\Delta Z_i$, $Z_i$ Electrical mobility step and electrical mobility

$\nu$ Kinematic viscosity

$\eta_{\text{tube,diff}}$ Diffusive particle loss in a tube

$\xi = \pi DL/Q$, a pipe flow parameter
1 Introduction

Why are people measuring small aerosol particles? Because they exist everywhere, they are diverse and complex and they interact with their surroundings. In the atmosphere their number concentration can vary from less than one to millions of particles per cubic centimeter. Their size varies from molecular clusters of around one nanometer in diameter to hundreds of micrometers. Their shape can be perfectly spherical or an extremely complex agglomerate and their color can vary from white to black. Their chemical properties vary and they can be mixtures of thousands of different molecular compounds.

All this makes aerosols extremely difficult to measure. For example no single particle sizing instrument is able to cover the whole size range from nanometers to millimeters and there still does not exist any satisfactory means to measure concentrations of particles around the nanometer size range. Also the chemical composition of atmospheric aerosol particles less than ten nanometers in diameter is virtually unknown. In many cases the unstable chemical composition of the particles leads to severe sampling artifacts. Particles can, for example, volatilize during the sampling.

The papers presented in this thesis mostly concentrate on particle concentration and size measurements. Together with particle chemistry they are the most important properties of aerosol particles. Aerosol particles are considered to be important, for example, because of their contribution to earth’s climate and people’s health.

It has long been known that increased concentrations of greenhouse gases such as carbon dioxide and methane can cause a significant warming of the earth’s atmosphere. A more recent finding is that aerosol particles can have a significant effect on the earth’s radiation balance [Charlson et al., 1992, Charlson et al., 1987]. Particles interact with the atmosphere by scattering radiation directly and by acting as seed particles in cloud forming processes. For both of these cases particle size and concentration are two of the most important factors. The intensity and pattern of scattered light from particles depends on the sixth power of the particle diameter and the saturation ratio needed to activate the growth of an aerosol particle to a cloud droplet is dependent on the particle mass (proportional to the third power of the diameter). The role of aerosols and clouds is the most uncertain factor in the field of climate change studies [Houghton et al., 2001].

Modelling of cloud formation is a difficult task mainly because it involves processes in a wide range of time- and space-scales. Cloud systems extend over thousands of kilometers lasting for weeks and droplet formation processes are triggered by aerosol particles some tens of nanometers in diameter in a few milliseconds. Cloud modelling requires the development of atmospheric aerosol dynamical models linked with chemical process models and meteorology. Cloud models are important not just for studying climate change but also for the stud-
ies of acid rain, photochemical smog production in the troposphere, and depletion of the ozone layer in the stratosphere.

Measurements of trace gases and aerosol concentrations are needed over wide spatial regions and over long periods of time to initiate and validate these models. Measurement campaigns like IAOE-91, ACE-2, BIOFOR and PARFORCE [Leck et al., 1996, Raes et al., 2000, Kulmala et al., 2001, O’Dowd et al., 2002] and the long term measurements in Hyytiälä and Värriö [Mäkelä et al., 1997 and Pirjola et al., 1998] have lead to a better understanding of particle formation and growth processes and the development of more accurate models like the ternary nucleation theory [Korhonen et al., 1999]. The development of nucleation theories especially rely on the good quality measurements of ultrafine particles. Development of new measurement methods with lower concentration and size detection limits and higher reliability is important.

Particles also interact directly with people. People can inhale, for example, harmful mine dust, diesel engine smoke or asbestos fibres. Air pollutants like ozone and particles have been associated with increases in mortality and hospital admissions due to respiratory and cardiovascular diseases [Brunekreef and Holgate, 2002]. It has been calculated that the famous 1952 London smog episode caused 12000 additional deaths. Mortality has been shown to increase by 0.6 % for each 10 µg/m³ increase in PM₁₀ (particle mass of particles less that 10 µm in diameter) and by 1.1 % for each 10 µg/m³ increase of black smoke. Ultrafine particles are also proposed to provoke alveolar inflammation which causes acute changes, for example, in blood coagulability [Seaton et al., 1995].

The aim of this study is to construct instruments to study the concentration, size distribution and dynamics of atmospheric ultrafine aerosols and instrumentation for cloud microphysical studies. This includes laboratory calibrations to verify the operation of the instruments, laboratory studies and long term field measurements to verify that these instruments are reliable enough to produce accurate data over long time periods. The measurements are used to evaluate the essential features of the atmospheric size distributions including the modal behavior of the distributions and to study, for example, formation and growth of the particles [Kulmala, 2003].

2 Particle instrumentation

Particle measurement systems consist of several units. One way to divide an online particle measurement system is: inlet, transport system, conditioner, analyzer and detector. This section is focused on ultrafine particle instrumentation. There are many definitions for ultrafine particles, but the most common definition is that they are particles smaller than 0.1 µm in diameter. The very small size of these particles causes several difficulties in sampling and analysis.
2.1 Inlets

The purpose of the sample inlet is to extract the particles under study from measurement volume and keep the undesirable particles out of the system. The inlet should be unbiased, e.g. it should work in both calm and windy conditions.

One example of a widely used inlet is specified as a part of the U.S. Federal Reference Method for PM$_{2.5}$ [Tolocka et al., 2001] (Figure 1). The inlet contains a curved top (1) and bottom plates (7) with a rain deflector (8) to keep the rain out. Between the top and bottom plates is a stainless steel mesh (5) (18x14 mesh) to keep insects out. A deflector cone (4) connected to the top plate steers the flow downwards. Below the upper section is the impactor nozzle assembly with drain water collection (not in the figure).

In freezing or condensing environments inlets are normally heated to prevent clogging, which means that they are also conditioning the aerosol. Heating is also preferable when the following stages of the sample treatment require low relative humidity conditions. One might, for example, want to sample hygroscopic aerosol in the dry state. Heating however, might affect the aerosol mass or chemistry and it is not recommended in the PM measurement guidelines (European standard EN12341).

Especially windy environments and aircraft measurements also require special
kinds of inlet design with directed and isokinetic inlets. Sometimes, on cloudy sites one might want to sample both interstitial aerosol as well as the activated droplets [Weingartner et al., 1999] or to get efficiently rid of large droplets like on the Finnish GAW station at Pallas [http://fmigaw.fmi.fi/]. The GAW program measurement guide clearly defines the inlets, particle transport and conditioning [http://www.wmo.ch/web/arep/gaw/publications.html] which should be used. In practice special local conditions sometimes overrule these principles.

In submicron particle measurements it is important to keep liquid water and large locally produced dust particles out of the system since they can cause real damage to the equipment and cause false results. In the publications included, a number of different inlet designs have been used. In papers I and II where measurements were made on a ship, a 10 µm Andersen high volume impactor was used as an inlet. In the other publications the inlets were not so well defined. Normally they were just 10 mm Stainless Steel tubing pointing down with a rain cover. In paper III on the Punta del Hidalgo site a vertical Stainless Steel tube 100 mm in diameter and 55 m long was used. The flow in the line was semiturbulent and the inlet was protected against rain.

2.2 Particle transport

Particles should be transported from inlet to analyzer without bias. However particles of different sizes penetrate sampling tubes with different efficiencies. For particles less than 100 nm in diameter the most important mechanism causing transport losses is diffusion. In tube flow the diffusive particle loss can be expressed as in Baron and Willeke, [2001]

\[
\eta_{\text{tube,diff}} = \exp\left( -\frac{\pi d L v_{\text{diff}}}{Q} \right) = \exp( -\xi Sh )
\]  

(1)

where \(d\) and \(L\) are the diameter and length of the tube respectively and \(Q\) the volumetric flowrate. Parameter \(v_{\text{diff}}\) is called the deposition velocity and \(Sh\) the Sherwood number. The Sherwood number is a dimensionless mass transfer coefficient given by \(Sh = \frac{v_{\text{diff}} d}{D}\), where \(D\) is the particle diffusion coefficient. Sherwood number is dependent on Reynolds number \(\left(Re = \frac{vd}{\nu}\right)\), gas velocity, \(\nu\) kinematic viscosity), which is the ratio of the inertial force of the gas to the frictional force and the Schmidt number \(\left(Sc = \frac{\nu}{D}\right)\), which describes the ratio between kinematic viscosity and the diffusion coefficient.

For laminar flow, when the friction forces dominate

\[
Sh = 3.66 + \frac{0.2672}{\frac{\xi}{0.10079\xi^{\frac{1}{3}}}}
\]

(2)

\[
\xi = \frac{\pi DL}{Q}
\]

(3)

10
One can see from the equation 3 that losses are dependent only on the particle diffusion coefficient (proportional to particle diameter), pipe length and flow rate. Hence, to minimize the losses one has to use as short pipes and as large flow rate as possible. Using short pipes is sometimes quite difficult since most recommendations say that sampling should take place from the free flow, 5 – 10 meters above obstacles. Also flow rate has an upper limit, since after the flow rate becomes turbulent (inertial forces start to dominate) transport losses increase substantially. In this case [Friedlander, 1977]

\[ Sh = 0.0118Re^{\frac{1}{3}}Sc^{\frac{1}{3}} \]  \hspace{1cm} (4)

When flow is turbulent diffusion losses become quite independent of the flow rate. The transition from laminar to turbulent flow happens after Reynolds number becomes larger than 2000. Table 2.2 lists some common flow rate pipe diameter combinations with \( Re=2000 \).

During the International Arctic Ocean Expedition (papers I and II) the sample flow was taken from the centerline of a plastic pipe, 5 m long and 9 cm in diameter. Flow was highly turbulent with a flowrate of 1130 LPM. In Punta del Hidalgo (paper III) the sampling line was ten times longer and semiturbulent. During the BIOFOR campaign (paper IV), some of the sampling lines were also very long (32 m and 82 m, 2.37 cm in diameter). Because of this, losses in these lines were determined experimentally beforehand. It was noticed that although flows were kept laminar, losses were larger than expected from theory. It seemed that surface roughness and bends in the lines increased transfer losses [Wang et al., 2002]. During other campaigns sampling lines were made of Stainless Steel or copper tube and have been 4 or 8 mm in diameter. Their length has always been minimized. Sampling lines should always be made of conductive material to avoid electrostatic deposition.

<table>
<thead>
<tr>
<th>Flow rate (LPM)</th>
<th>Pipe diameter (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.4</td>
</tr>
<tr>
<td>12</td>
<td>0.8</td>
</tr>
<tr>
<td>16.67</td>
<td>1.2</td>
</tr>
<tr>
<td>30</td>
<td>2.1</td>
</tr>
<tr>
<td>100</td>
<td>7</td>
</tr>
<tr>
<td>143</td>
<td>10</td>
</tr>
<tr>
<td>220</td>
<td>15</td>
</tr>
<tr>
<td>286</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 1: Flow rate and tube diameter combinations with Reynolds number 2000
2.3 Conditioning

In many cases aerosol conditioning can not be avoided. For example in cold climates it is difficult to avoid warming the aerosol, which also effects the aerosol relative humidity. By heating the sample the most volatile part of the aerosol might partly or completely evaporate, which will cause bias to sampling. In most cases, however conditioning is desirable. The most common types of conditioning are dilution and the removal of water vapor and liquid water. For electrical mobility based instruments, it is necessary to bring the sample to equilibrium charge distribution using a radiation source.

Dilution is used when the particle concentration or the relative humidity is too high for the instrument. Many kinds of dilution systems are described in literature. The most common ones are capillary tube diluters (TSI-3302, TSI Inc.), ejector diluters (Dekati DI-1000, Dekati Ltd and Palas VKL-10, Palas GmbH) and several types of mixing tanks or nozzles [Baron and Willeke, 2001, Brockmann et al., 1984, Hueglin et al., 1997]. In all dilution devices it is important to know the exact dilution ratio and that the ratio does not change with parameters like pressure and temperature.

When particle size distributions are presented in literature in most cases measurements are made in the dry state (RH less than 30 %). If they are made in ambient humidity, it is normally explicitly mentioned. There are several ways to decrease aerosol humidity. The most effective way is to dilute the sample with dry particle free air. Other ways are Permapure driers (Permapure Inc.) or special aerosol diffusion driers (TSI-3062, TSI Inc. or Topas-DDU 570/L, Topas GmbH). These driers can cause large diffusional losses. These losses have been studied experimentally. Losses in the model MD-070-24S-4 Permapure drier are equivalent to the losses in a two meter long tube and losses in the Topas drier are equivalent to the losses in a five meter long tube with laminar flow.

Particle charge neutralization is especially important when working with Differential Mobility Analyzers (DMA), because their usage relies on a known charge distribution of the aerosol. Normally in atmospheric sampling, the aerosol is brought to charge equilibrium by diffusion charging with $\beta$ or $\alpha$ radiation. Many different radiation sources are used e.g. $^{85}$Kr, $^{241}$Am, $^{210}$Po and $^{63}$Ni. The most common ones are TSI-3077 $^{85}$Kr 2mCi source and various $^{210}$Po sources used for static electricity removal. Polonium neutralizers are typically more effective than krypton neutralizers. The disadvantages with $^{210}$Po are it’s short half-life (138 days) and like with all the $\alpha$–emitters a risk of producing small particles [Covert et al., 1997]. Soft X-ray sources have also been used for ion production in neutralizers [Shimada et al., 2002].
2.4 Detectors

The detector is the device which is used to count the number of particles in a defined volume. A perfect detector will detect all the particles over the whole size range from molecular clusters to rain droplets and at all concentrations. Ultrafine particles can be detected with two methods; either measuring the current delivered by a flow of charged particles to a Faraday cup by an electrometer or by condensing vapor on them and growing them to larger sizes where they can be detected with optical methods.

2.4.1 Condensation Particle Counter

Condensation Particle Counters (CPC) are instruments where small particles are grown to optically detectable sizes by condensing some vapor on them. Condensation particle counters have been used in aerosol science for over a hundred years. Reviews about the subject have been written, for example, by Spurny [Spurny, 2000] and McMurry [McMurry, 2000].

There exist three main types of CPCs: laminar flow, mixing-type and expansion-type CPCs. The most common one is the laminar flow CPC where the condensation growth is achieved by forced convection. The first kind of CPCs of this kind were designed during the 70’s by Rosen [Rosen et al., 1974], Bricard [Bricard et al., 1975] and Sinclair [Sinclair and Hoopes, 1975a]. Rosen’s instrument was a thermal gradient diffusion cloud chamber using water as the condensing species. Bricard’s and Sinclair’s instruments used a warm saturator followed by a cold condenser where the growth started. These two instruments employed alcohols as the condensing vapor. Alcohols are used mainly because their vapor pressure is high enough that particles grow to detectable sizes and their diffusivity is low enough to prevent the vapor to diffuse too fast to the walls. The first commercial instruments by TSI were designed by Agarwal and Sem in the beginning of the 80’s. A good review about TSI instruments is given by Gilmore Sem [Sem, 2002]. The first TSI model, 3020 was replaced almost ten years later by TSI model 3022. This instrument uses butanol as a working fluid. In standard configuration the CPC’s minimum detectable diameter (50 % cut size) is seven nanometers and flow rate 0.3 LPM. The instrument’s maximum detectable concentration is $10^7$ cm$^{-3}$. The TSI model 3025 was based on a design by Stolzenburg [Stolzenburg and McMurry, 1991]. This instrument was designed to lower the smallest detectable particle diameter by feeding the aerosol into the middle of the condenser tube to achieve more uniform supersaturation for all the particles. With this design the detection threshold came down to three nanometers in diameter, but with the drawback of a very low sample flow rate (0.03 LPM), decreasing the counting statistics with low concentrations. TSI has also developed more compact CPCs like the model 3010 [Keady, 1988]. Since these instruments are widely used, many calibration studies have been presented in the literature [Agarwal and
Another type of steady-flow instrument is the mixing-type CPC. In these instruments cold aerosol flow is turbulently mixed with hot vapor and then cooled rapidly. Typical working fluids are water and different oily substances like di-Octyl-Phtalate (DOP). The first of these kind of instruments were built in Russia by Kogan and Burnashova, [1960] followed by Sutugin and Fuchs, [1965], Okuyama et al., [1984], Ankilov et al., [1991] and Mavliev, [2002]. There exists one commercial instrument of this type (Kanomax model 3851), but they are not widely used. The advantages of these instruments are, that they can be easily designed to have very low diffusional losses and small detectable sizes. They can also handle large sample flow rates. Sgro and de la Mora, [2004] have demonstrated that mixing-type CPCs can be used to count also small ions.

The first CPCs used were expansion-type instruments, where sufficient supersaturation is achieved by rapid adiabatic expansion. These devices were initially developed in the late 19th century by Coulier and Aitken. They used devices where particle concentrations were calculated by visually counting the particles at the collection stage. The most famous device of this type was Aitken’s Pocket Dust-Counter [Aitken, 1890]. Later, more automatic counters were developed. A widely used automatic counter is the Model 1957 Pollak counter [Metnieks and Pollak, 1959]. It is still used, for example, at some Global Atmospheric Watch (GAW) stations daily. Several commercial instruments were developed from the devices developed in the General Electric Research Laboratories for military purposes during the 1950s. One of them is still commercially produced, Rich-200 by Environment/One.

At the University of Helsinki numerous CPCs have been calibrated prior to and after the field campaigns. Figure 2 shows the instrument calibration system used. Particles are generated in a nitrogen atmosphere by heating bulk material with a tube furnace followed by cooling, which initiates the nucleation of the produced vapor. The size and concentration of the particles produced depends on the oven temperature, flow rate through the furnace and the efficiency of the cooling. In most calibrations silver has been used as the particle material. Silver is chosen because it is inert and the particles produced are spherical for particle diameters smaller than 20 nm [Augustin, 1996]. The nitrogen atmosphere is necessary to prevent oxidation. The furnace temperature is typically varied between 900 °C and 1200 °C which corresponds to a particle mean diameter range from 3 to 25 nanometers. The particles produced are neutralized with an $^{241}$Am alpha emitter.

The particles are classified with a Hauke Differential Mobility Analyzer (DMA), which selects a monodisperse fraction of the size distribution. The aerosol flow rate has typically been 2 LPM and the sheath flow rate 20 LPM. With these flow rates, the half width of the size distribution centered to three nanometers is around half a nanometer. Due to the fact that the classified particle distribution
Figure 2: University of Helsinki laboratory calibration system

is not exactly monodisperse, one must take care that the original particle size distribution produced with the furnace should be quite flat around the classified particle mean diameter. An error of 0.2 nm in classified mean diameter can easily occur if the original particle distribution mean diameter differs considerably from the classified mean diameter. After the classification the aerosol is diluted using a dilution loop and it’s concentration is measured with an aerosol electrometer (TSI model 3068) and with the system under calibration. As an example, Figure 3 shows a detection efficiency calibration of some TSI CPCs. The model 3025 has the lowest cut size, 2.6 nanometers and the model 3760 the highest 16.5 nm. The model 3010 with a 25 °C temperature difference between the saturator and condenser and the model 3022 have almost the same cut sizes, 5.8 nm, although the model 3010 has a steeper calibration curve than the model 3022 indicating lower diffusion losses. The portable model 3007 has a cut size of 10.0 nm. In the calibrations made for papers I and II, the calibration system was fairly similar to the one described above. The main difference was, that sodium chloride was used as the particle material. Sodium chloride particles tend to be cubical as opposed to silver particles, which are spherical. For paper IV the TSI-3025s and TSI-3010s used during the BIOFOR campaign were calibrated with the system described above. For paper VI two particle generation systems were used in parallel. The first, similar to the one described above was used to produce 20 nm silver particles, which were used as reference particles. In the second system a nebulizer was used as an aerosol generator to produce the required sub 10 nm salt particles. The problem with nebulizers is, that the yield of sub five nanometer particles is very small.
2.4.2 Electrometer

Electrometers are devices, which measure the current or the accumulation of charge produced by charged aerosol particles. Electrometers are typically used in instruments where the particle size distribution is measured using electrical mobility techniques. Such kind of instruments are, for example, Electrical Aerosol Analyzer (EAA) [Liu and Pui, 1975], Electrical Mobility Spectrometer (EMS) [Winklmayr et al., 1991] and Electrical Aerosol Spectrometer (EAS) [Tammet et al., 2002]. The Electrical Low Pressure Impactor (ELPI) also uses electrometers for particle detection even though the particle classification is performed by an impactor [Keskinen et al., 1992]. The limitation of these devices is their sensitivity. Electrometers used in these devices current have noise levels of around a fA. The EAS has the lowest reported noise level, 0.05 fA. For 50 nm particles the ELPI and EMS have minimum detection limits of 130 cm$^{-3}$ and 200 cm$^{-3}$ respectively.

2.5 Analyzers

2.5.1 Differential Mobility Analyzer

A Differential mobility analyzer (DMA) is an instrument where charged particles are classified according to their electrical mobility. The analysis is differential...
since only a small mobility fraction is classified at a time.

Mobility analyzers have been used for as long as CPCs and a good historical review is given by Flagan [Flagan, 1998]. The development of DMAs commonly used today started with the work of Liu and Pui from the University of Minnesota [Liu and Pui, 1974, Knutson and Whitby, 1975]. They modified the instrument, designed earlier by Hewitt [Hewitt, 1957] and used it for instrument calibration by producing monodisperse particles with it. A theoretical description of it’s performance has also been published by Knutson and Whitby [Knutson and Whitby, 1975]. The commercial version of this instrument is still used today (TSI model 3071 DMA). Later, new DMA types were developed. The University of Vienna DMA is an instrument optimized to minimize particle losses in the inlet and outlet [Winklmayr, 1991]. This DMA type has been manufactured, for example, in Germany, Sweden and Finland. The commercial version has also been available. The TSI DMA was redesigned for smaller particle sizes by Chen et al., [1998]. The DMA column was shortened from 444 mm to 50 mm, inlet and outlet lines were reorganized and an additional outlet was added to increase the aerosol inlet flow and thus decrease the losses in the inlet. In all these models the electrodes are cylindrical. Two new radial DMA types were developed by Zhang and Pourprix during the mid 1990’s [Zhang et al, 1995, Fissan et al., 1998]. In these models the aerosol flows radially between two round plate electrodes.

Knutson and Whitby introduced an idealistic theoretical description of the DMA performance. Later, Stolzenburg introduced a correction which took into account the diffusion of small particles inside the DMA column [Stolzenburg, 1988]. Diffusion leads to the broadening of the ideal transfer function. The calibration experiments made, for example, by [Stolzenburg, 1988, Fissan et al., 1996, Birmili et al., 1997, Reischl et al., 1997, Chen et al., 1998 Fissan et al., 1998, Martinsson et al., 2001, Karlsson and Martinsson, 2003] are in fair agreement with theory. Another issue that has to be taken into account in DMA measurements are the losses in the DMA inlet and outlet. For example, the TSI 3071 has losses equivalent to a 13 metre long tube with laminar flow [Soderholm, 1979]. Between different calibrations there exist some disagreement. For ten nanometer particles with an aerosol flow rate of 1 LPM the penetration efficiency calculated from Soderholm data is 0.52, from Birmili data 0.57, from Karlsson data 0.65 and Fissan data 0.25. In our calibrations ten nanometer penetration efficiency has been around 0.45.

Figures 4 and 5 show a typical calibration of a 10.9 cm long Hauke DMA constructed in the University of Helsinki. In the first figure, 400 nm PSL particles are used to test the sizing accuracy of the DMA. The mean particle size is approximately 400 nm. The small difference can be explained by a deviation in the DMA sheath flow. The second figure presents the penetration efficiency calibration for the DMA. The calibration system was similar to that in Figure 2. Silver particles were produced with a tube furnace and classified with a DMA. The particle concentration downstream of the first DMA \(N_1\) was measured with
Figure 4: Calibration of Hauke DMA with 400 nm PSL particles

A TSI model 3025 CPC and its mobility distribution \( n_2(Z_i) \) was measured with the DMA under calibration and a TSI 3025 CPC. The penetration efficiency \( \lambda \) is calculated using

\[
\lambda = \frac{Q_s}{Q_a N_1} \sum_i n_2(Z_i) \frac{\Delta Z_i}{Z_i},
\]

where \( Z_i \) is electrical mobility, \( \Delta Z_i \) the electrical mobility step used in the calibration, \( Q_s \) sheath flow rate and \( Q_a \) aerosol flow rate [Karlsson and Martinsson, 2003]. The diffusional losses of the DMA are equivalent to five meters of tubing with the same laminar flowrate. The penetration efficiency does not reach unity for large particle diameters indicating some electrostatic losses in the DMA outlet. Some diffusional broadening of the DMA transfer function can be seen (Figure 5) with the smallest particle diameters used.

A DMA can be combined with a neutralizer and a CPC to create a Differential mobility particle sizer, DMPS [Hoppel, 1987] or a Scanning mobility particle sizer (SMPS) [Wang and Flagan, 1990]. This device measures particle size distributions by detecting the particle concentration with a CPC after the DMA with different DMA voltages. The voltage of the DMA can be changed step wise (DMPS) or continuously (SMPS).

The University of Helsinki’s differential mobility particle sizer is shown in Figures 6 and 7. It was used, for example, during the campaign described in paper IV and also for continuous measurements [Mäkelä et al., 1997]. Air is sampled via an inlet through the roof. The inlet is shielded with a rain cover and
Figure 5: Penetration efficiency calibration of Hauke DMA. The circles in the first figure present the raw penetration efficiency data and the solid curve presents the laminar flow particle losses in a tube with a length of 5 meters. Second picture shows the raw calibration data.

the sample is dried with a Permapure drier. After drying the aerosol is neutralized with a 370 MBq $^{63}$Ni radioactive source. The sample is then divided into the two DMPS systems. The first is equipped with a TSI-3025 particle counter and a 109 mm long Hauke-type DMA. The second has a TSI-3010 particle counter and a 280 mm long DMA. The first DMPS measures the particle size distribution from 3 to 15 nm and the second one from 15 nm up to one micrometer. The number of size channels measured in the first DMPS is typically less than ten, in order to maximize the counting statistics as ultrafine particles are charged very inefficiently (Just a few percent of the sub ten nanometer particles are charged). The aerosol flow rate of the TSI-3025 is also low which further decreases the certainty. For the second DMPS, thirty channels are commonly used. The larger particles have a higher probability of carrying a charge and the aerosol flow rate of the TSI-3010 is more than thirty times larger than that of the TSI-3025. The sheath flows are arranged as closed loops, the excess flow is used again as a sheath flow. The sheath flows controlled with critical orifices are dried and filtered. The DMPS system used during the IAOE-91 campaign (papers I and II) was essentially similar to the one in Figure 6. The Permapure drier was not used because in the cold climate, the relative humidity inside the DMPS is much lower than ambient due to the temperature increase from ambient to room temperature. Sheath flows were not arranged as a closed loop. A separate compressor and vacuum pump were used for the sheath and excess flows respectively.
To get the particle size distribution \( dN/d\log D_p \) from the raw data which is concentration vs. voltage, one has to know the charge distribution of the aerosol, DMA transfer function, detection efficiency of the CPC and losses in the sampling lines. For the charge distribution, semi-empirical equations are normally used like the one published by Wiedensohler [Wiedensohler, 1989]. For the DMA transfer function, equations by Stolzenburg are quite commonly used [Stolzenburg, 1988]. Transformation from voltage-concentration space to diameter-concentration space is called inversion. For normal atmospheric DMPS measurements the inversion is fairly stable and simple pseudo-inversion algorithms can be used [Golub and Van Loan, 1996]. One can also force the size distribution to just have positive values by using methods like nonnegative least squares (NNLS) [Lawson and Hanson, 1974]. If the result of the inversion seems to be very unstable, different regularization methods might help. One commonly used method is the Tikhonov regularization with the L-curve algorithm to regularization parameter estimation [Hansen, 1998].

In paper I, the extreme value estimation (EVE) method was used as an inversion method [Paatero, 1991, Aalto et. al, 1990]. In the paper it was used to invert DMPS, diffusion battery and Pulse Height Analysis Ultrafine Condensation Particle Counter (PHAUCPC) measurements. Originally EVE was written to invert exponential curves like those produced by diffusion battery. Like all the methods mentioned above, EVE deals with the inversion of the linear model.

\[
b = Ax + e
\]  
\[b = Ax + e\]  

In the equation above, \( b \) contains the measured spectra, \( A \) the model matrix of the instrument used, \( x \) the unknown coefficients and \( e \) is the error term. As a first step EVE finds the non-negative values of \( x \) so that the so called chi-squared value \( q \) gets it’s smallest possible value.

\[
q = \sum_i \left( \frac{e_i}{s_i} \right)^2
\]  
\[q = \sum_i \left( \frac{e_i}{s_i} \right)^2\]

The variable \( s \) is the predefined error for the coefficients in the vector \( b \). In the second phase EVE tries to find the set of acceptable solutions for the linear equation, so that the set of solutions contains the unknown correct solution with high probability (90-95 %). The idea behind EVE is that no solution among the acceptable solutions is better than any other. EVE is normally used to estimate some functions of the unknown variable \( x \). These could be, for example, window sums and peak parameters (height, position and width). Some problems are more ill-posed and unstable than others and require some auxiliary information to be solved meaningfully. This extra information included could be, for example, a limit for the smoothness of the solution. With particle size distributions one could say that the minimum geometric standard deviation is 1.2. The smoothness of the solution can be achieved with EVE using two-stage modelling.

20
Figure 6: Schematic picture of the University of Helsinki DMPS

Figure 7: University of Helsinki DMPS on the field
2.5.2 Cloud Condensation Nucleus Counter

Cloud Condensation Nucleus Counters (CCNC) are commonly used to study particles ability to act as seed particles for cloud droplets. In the atmosphere, cloud droplets are formed in low supersaturation conditions caused by updrafts. Typical water supersaturation achieved in the atmosphere is between 0.05 % to 0.8 %. Smallest supersaturations are typical for stratiform clouds and largest for cumulus clouds [Seinfeld and Pandis, 1998].

Most CCNCs are diffusion cloud chambers. In these devices supersaturation is achieved between two parallel moist plates kept at different temperatures. A temperature difference of five degrees produces one percent water supersaturation. Another type of instrument is the isothermal haze chamber, where critical supersaturation is calculated by measuring the particle size distribution at 100 % humidity.

Diffusion cloud chambers can be divided into three subgroups: static, continuous flow and dynamic cloud chambers [Nenes et al., 2001]. The oldest type is the static thermal diffusion cloud chamber [Twomey, 1963]. Firstly, particles are rapidly fed into the diffusion chamber. After a time the chamber settles to equilibrium and the particles begin to grow. The CCN concentration is measured by counting the number of droplets formed. This counting is the difficult part of the process. In the first instruments developed, droplets were counted manually with a microscope. Currently, photoelectric methods or video cameras are used. Static chambers do not operate continuously, since it takes some time to fill the chamber. Filling the chamber also causes supersaturation transients which should be taken into account. The lowest usable supersaturation in this type of instrument is around 0.2 %. An improvement of the original version is the continuous flow parallel plate diffusion chamber. As the name suggests, flow through the chamber is continuous and the concentration can be recorded continuously, either with photoelectric methods inside the chamber or by feeding the sample into an optical counter outside the chamber [Sinnerwalla and Alofs, 1973]. This type of chamber is described in papers III and V. The advantages of this type of instrument are continuous recording, a uniform supersaturation field near the centerline and the lack of transient supersaturations if properly designed. One can also achieve slightly lower supersaturations with this instrument type compared to static chambers. The third type of instruments are the dynamic CCN spectrometers. The idea behind these instruments is to instantly record the whole supersaturation spectra between 0.01 to 1 % by measuring the size spectra of the formed droplets after the flow chamber. The most frequently used type of this instrument is Hudson’s dynamic spectrometer [Hudson, 1989]. This instrument is a continuous flow chamber with an increasing temperature difference in direction of the flow between the parallel plates. Particles with different critical supersaturation are activated in different segments. Due to the different growth times the final droplet sizes diverge.
The main problem of existing CCNCs is that they are mostly prototype laboratory instruments. The only commercial counter in use, is the DH Associates model M1 static chamber, which is used, for example, at the Mace Head GAW station. A comprehensive intercomparison between different instruments was carried out twenty years ago in Reno [J. Rech. Atmos. 15]. Four isothermal haze chambers were studied over the critical supersaturation range of 0.01 to 0.2%. Two of them agreed within 40% over the whole range. The third agreed with the first two over the lower part of the critical supersaturations. The fourth was not working well during the experiment. Nine static diffusion chambers were studied. Five of them agreed with each other to within 20%. The others were not operating so well. The four continuous flow diffusion chambers tested, agreed within 15% in most cases and were clearly the most reliable instrument type.

The construction of the first version of the University of Helsinki CCN chamber was started in 1993. The construction process is documented in three conference abstracts [Aalto and Kulmala, 1993, Aalto et. al, 1994 and Aalto, 1995]. The dimensions of the first chamber were almost the same as in the second version documented in paper III. The main differences were the temperature control of the chamber walls, which was achieved in the first version with thermoelectric devices and the aerosol sampling. In the first version droplets were sampled from the centerline of the chamber. The counting efficiency of the CCN chamber depends on the flow rate and the supersaturation. For different supersaturations there exists an ideal flowrate with which the activated droplets do not grow enough to be deposited inside the chamber or, at least, so little that they could not be detected with the optical counter. For 0.2% supersaturation the optimal flowrate was 2 LPM and for 1% supersaturation 5 LPM, with corresponding
growth times of between eight and twenty seconds, respectively. The accuracy of the supersaturation set point was tested by measuring the critical diameter of the monodisperse sodium chloride particles. The result of the experiment is presented in Figure 10. The test showed that the supersaturations were slightly lower than expected.

The second version of the instrument was built for the ACE-2 campaign. The thermoelectric wall temperature controls were replaced with a water circulation system controlled by two heat baths to achieve more accurate control of the temperatures. The flow system was also changed. Aerosol particles were fed on the centerline of the chamber instead of sampling them from the centerline. This change was later proven to be difficult to implement. The aerosol was rapidly mixed with the clean sheath flow and aerosol particles experience a range of supersaturations from zero to maximum. The mixing also led to an increase in deposition losses. Figures 8 and 9 present this version during the campaign presented in papers IV and V. At the center of the Figure 9 is the actual CCN chamber. The chamber walls are kept at constant temperatures by heat baths located on the outside. Temperatures are measured with PT-100 temperature sensors. On the right is the optical counter which detects the droplet concentration after the chamber. On the left is the DMA-CPC system which is used to classify the particles and measure their concentration before they are fed into
the CCN chamber. Figure 11 shows the test of supersaturation accuracy. The critical diameters measured by the second version of the chamber were in better agreement with the diameters calculated from Köhler theory.

2.5.3 Pulse Height Analysis Ultrafine Condensation Particle Counter

During the 80’s Brockmann, [1981] and Stolzenburg, [1988] noticed that the final droplet size in the TSI-3020 and the prototype TSI-3025 (Figure 12 and 13) was dependent on the initial particle size. The pulse heights observed from the optical particle counter were smaller for the ultrafine particles than for the larger particles. They argued that due to the Kelvin effect, smaller particles have to travel further into the condenser to get activated and have subsequently a shorter time to grow and thus a smaller final droplet size. The Pulse Height Analysis Ultrafine Condensation Particle Counter (PHAUCPC) was first used during the International Arctic Ocean Expedition (papers I and II). During the expedition an alternating condenser temperature technique was also tested with the same instrument. Of these two techniques the pulse height method was the more reliable with the instrument used. Later Saros et al., [1996] calibrated the instrument with tungsten oxide, sulfuric acid and sodium chloride, Marti et al, [1996] showed how to modify the standard TSI-3025 to achieve pulse height analysis capabilities. Weber et al., [1998] investigated the data analysis of the pulse height data and used the instrument during the ACE-1 campaign [Weber et al., 1997]. Saros also
Figure 12: Prototype TSI-3025 ready to be shipped to the Arctic.

Figure 13: Flow schematics of the TSI-3025 [Instruction manual, TSI Incorporated].
speculated that the difference observed between the NaCl and (NH$_4$)$_2$SO$_4$ calibration occurred due to the cubical shape of the sodium chloride crystals. Later, it was shown by Hanson [Hanson et al., 2002] that sulfuric acid calibrations made by Saros were disturbed by ammonia contamination and the instrument response depends also on the chemical composition of the aerosol. Already in 1979, it was published that the CPC calibrations with sulphuric acid differ from the sodium chloride calibrations [Madelaine and Metayer, 1980]. In paper VI this finding was used in investigations of the ultrafine particle composition.

During the third Biofor campaign in Hyytiälä in 1999 it was noticed that the concentration of particles smaller than six nanometers in diameter measured with the University of Helsinki’s DMPS and the University of Minnesota’s PHAUCPC differed by more than one order of magnitude. At that time it was speculated that the calibration of the PHAUCPC is dependent on the particle composition. During spring 2000, the measurements were repeated with the same DMPS and the National University of Ireland, Galway’s PHAUCPC and the instrument was recalibrated with organic particles. The results for a particle size of five nanometers with different particle compositions is presented in Figure 14. In each curve there exists two peaks. The peak in channel 800 is the reference peak produced by large silver particles. All the particles larger than ten nanometers produce peaks centered at the same channel. The peak on the left is the five nanometer particle peak. The calibration with silver particles is very similar to the calibration...
presented in paper I and in the paper by Saros. However the calibrations with organic acids differed considerably from the standard silver calibrations. This difference could explain the measurements made in Hyytiälä. Observed particles are soluble in butanol and grow forming solution droplets before the actual activation. The ammonium sulphate calibration differs also from the silver calibration. The reason for this is unknown, but could be explained by particle evaporation.

2.5.4 Diffusion battery

For diffusion battery measurements three assumptions are employed in the size classification of particles. Small particles are affected by collisions with gas molecules. The amount of Brownian motion caused by these collisions is a function of particle size. Particles are tightly bound to any surfaces they impact. A diffusion battery can be, for example, a series of tubes where small particles diffuse to the walls of the pipes as they flow through them. This deposition leads to a decrease in the concentration. The rate of the decrease is a function of the particle diameter. When the concentration is measured at several points downstream in the tube, the particle size distribution can be calculated using special inversion techniques.

Many types of diffusion batteries have been developed during the last decades: parallel plate, cylindrical tube, collimated hole, stacked filters, wire screen and packed beds. A good review of diffusion batteries and their use is given by Knutson, [1999]. In many cases constructing a compact structure with a lot of surface where particles can diffuse has been problematic. The wire screen diffusion battery instrument described by Sinclair and Hoopes, [1975b] is one of the easiest to build and TSI started to manufacture it in 1976. The main problems with diffusion batteries have always been their limited size resolution, difficult data inversion and sensitivity to concentration oscillations. Many authors have concluded that equal-amplitude peaks can be resolved if their modal diameters differ by more than a factor of three. The data inversion problems have led to hundreds of articles being published including [Aalto et. al, 1990].

As stated in paper I, a diffusion battery was also used during IAOE-91. The instrument was a shortened version of the TSI-3040S described by Sinclair and Hoopes. The instrument was shortened in order to achieve better time resolution. Although the instrument produced good data for the ultrafine particles, the data was not used much in the followup papers. The main reason for this was the limited size resolution. The DMPS data was more valuable in studies of modal structure, growth and production of the aerosol particles. Later, the full length TSI diffusion battery was used during University of Helsinki field campaigns in Finnish Lapland [Aalto et. al, 1992, Aalto et. al, 1995 and Pirjola et. al, 1998] and near Helsinki [Hämeri et. al, 1996].
3 Review of the papers

The papers reviewed here are based mostly on measurements performed during two large measurement campaigns, the International Arctic Ocean Expedition (IAOE-91) [Tellus 48B] and Biogenic Aerosol Formation in the Boreal Forest (BIOFOR) [Tellus 53B]. In paper III data from other campaigns is also used. These are, for example, the 2nd aerosol characterization experiment (ACE-2) [Tellus 52B] and Particle Formation and Fate in the Coastal Environment (PARFORCE) [Journal of Geophysical Research 107, D19]. Paper VI is a direct successor of the BIOFOR campaign results with more detailed measurements.

Paper I describes the operational principles and characteristics of the four instrumentation types used during IAOE-91. The use of these instruments became possible because of the brand new instrument manufactured by TSI, TSI model 3025 ultrafine condensation particle counter. Two of the instruments used were already quite familiar to the aerosol community, the DMPS and diffusion battery technique. The new particle counter just extended their possibilities. The two other instruments, the PHAUCPC and the variable condenser temperature method were used for the first time in the field. In the paper all the instruments used are calibrated except the DMAs, field data is used to intercompare the methods and the instrument resolutions are studied.

Paper II is an aerosol number size distribution characterization paper based on results from the IAOE-91 campaign. It describes the instrumentation used and gives an estimate of the reliability of the dataset. It presents the modal structure of the aerosol size distributions measured and their frequency of occurrence. It is one of the first papers where the ultrafine particle mode is described.

Paper III is a summary of the measurements made with the University of Helsinki’s CCN counter. It describes the instrument in its various configurations, presents a method to calculate a particle’s soluble fraction from its measured critical diameter and presents field data. The article shows the average CCN behaviour and calculated soluble fractions at the Hyytiälä site, two marine sites and an urban site.

Paper IV is the aerosol number size distribution characterization paper of the BIOFOR campaign. It includes a calibration section and a results section describing again the modal structure of the size distributions. It also contains some analysis of the particle production events. It gives some conditions during which small particle production is probable. Vertical concentration gradients were also discovered during the particle production events. The small particle concentration difference between DMPS and PHAUCPC instruments was recognized
during these measurements which led to paper VI.

**Paper V** introduces the aerosol hygroscopicity characterization based on results from the BIOFOR campaign. It contains soluble fraction comparisons calculated both from tandem differential mobility particle sizer (TDMA) data and CCNC data. Two TDMA (University of Lund and University of Helsinki) are compared to each other. The most interesting finding of this paper was the diurnal variation of the particle solubilities.

**Paper VI** is a brief paper describing the PHAUCPC measurements made at the Hyytiälä station during spring 2000. It is a follow up paper to paper IV where a discrepancy between the DMPS and PHAUCPC measurements was found. In the paper it was proposed that the difference is possibly due to the organic nature of the ultrafine particles.
4 Summary and conclusions

This thesis presents details of the construction and calibration of instruments used for atmospheric ultrafine particle measurements. The measurement range of the DMPS has been extended down to three nanometers and more reliable DMPS systems have been constructed for long-term measurements (Papers I, II and IV). When particle concentration is high enough, the DMPS equipped with the TSI model 3025 and with any DMA designed for ultrafine particle measurements, provides the best size distribution information. However due to low aerosol flow rate of the TSI 3025 CPC and the low charging probability, concentration of particles less than ten nanometers on diameter has to be more than 100 cm$^{-3}$ to be detected with a good certainty. A new ultrafine CPC with a aerosol flow rate of 5 LPM would considerably improve the detection limit. More efficient aerosol chargers would as well make the detection of nanoparticles easier. The smallest particle size the DMPS can detect is limited by the detection limit of the TSI 3025 CPC. Smaller particles can be detected by high flow rate ion spectrometers equipped with sensitive electrometers like the ones produced in the Air Electricity Laboratory, University of Tartu [Hörrak et al., 2003].

A completely new instrument for small particle measurements, the PHAUCPC has been constructed, calibrated and tested in the field (Papers I and II). It has been used to measure the concentration of particles less than eight nanometers in diameter. The PHAUCPC is at this moment the most sensitive instrument for nanoparticle concentration measurements. It can easily detect nanoparticle concentrations less than 0.1 cm$^{-3}$ corresponding at least three orders of magnitude better detection limit compared to the DMPS. However the calibration of the PHAUCPC is dependent on the particle composition, making the interpretation of atmospheric measurements difficult. This dependency is also an advantage. The PHAUCPC has been used together with the DMPS to study the solubility of ultrafine particles in butanol. By studying the particle solubility, information about the ultrafine particle chemical composition can be derived (Paper VI). There is a lot of possibilities for improvements in the PHAUCPC design. The supersaturation profile inside the PHAUCPC condenser could be optimized to achieve improved particle size resolution and range. With a use of different working fluid the effect of particle solubility could be reduced. As well more detailed composition information could be attained by using variety of working fluids.

A CCN counter has been constructed, tested and used in the field (Papers III and V). The highest soluble fractions were detected on the two marine sites in Tenerife and in Mace Head, Ireland. The lowest soluble fractions were detected on the boreal forest site in Hyytiälä, Finland. On the urban site in Helsinki, Finland the soluble fractions were typically between the marine and boreal forest site readings. By using the estimated particle soluble fractions calculated from the CCN counter and the Tandem Differential Mobility Analyzer (TDMA) data these two instruments have been compared. The overall agreement between the
two instruments seemed to be fairly good indicating that it doesn’t make any difference whether the soluble fraction measurements are done in 90 \% humidity or at water supersaturation. With the CCN chamber constructed there exists a lot to improve. The flow arrangement should be completely redesigned to prevent the undesirable circulation of the aerosol flow. Also the deposition losses should be decreased. The easiest solution might be to return to the flow arrangement of the first prototype and sample the aerosol from the centerline of the chamber. The inlet and outlet parts should be also redesigned to prevent recirculation of the flow. To decrease the deposition the chamber could be tilted so that the flow direction is vertical instead of the current horizontal flow direction. At least gravitational deposition should decrease with this arrangement.

The instruments constructed have been used during measurement campaigns in the Arctic during IAOE-91 and AOE-96 [Journal of Geophysical Research 106, D32], Finnish Antarctic measurement station ABOA [Koponen et al., 2003], the Subarctic station of Värriö in Lapland, the boreal forest in Hyytiälä, Finland, Helsinki and other cities in Finland, the coastal site in Mace Head, Ireland, the German site in Melpitz, Mediterranean sites in Athens and Marseilles and a marine site on Tenerife, Spain. The essential features of the size distributions like the modal behavior and evolution are described. Three or four distinct number modes were found in the boundary layer. In the Arctic region (Paper II) their geometric mean diameters were 14 nm, 45 nm and 170 nm referred to as ultrafine, Aitken and accumulation modes. The lowest total concentration detected was around $0.5 \text{ cm}^{-3}$ and mean concentration around $100 \text{ cm}^{-3}$. During the AOE-96 the accumulation mode mean diameter was 130 nm and Aitken mode mean diameter varied between 15 and 60 nm. Ultrafine particle mode was detected within more than twenty days during the seventy day expedition. Total concentration varied between 5 and $5000 \text{ cm}^{-3}$. In the boreal forest (Paper IV) two dominant modes were found with mean diameters of 44 nm and 154 nm. During sunny, low surface area days ultrafine mode was detected typically in the late morning. The mean diameter of the ultrafine mode was at first below the detection limit and grew during the day into the Aitken mode sizes. Coarse mode was detected having volume mean diameter of 2.0 \( \mu \text{m} \). Total concentration varied between 410 and $45000 \text{ cm}^{-3}$.

The instruments constructed have revealed new information about new particle production in the atmosphere even though the detection is limited to approximately three nanometers. New data is also produced for studies of aerosol dynamics, condensation and coagulation processes in the atmosphere.
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