

Measurement of nucleation mode particles using an ultrafine water-based condensation particle counter

E. Filimundi^a, O.F. Bischof^b, I.P. Bennett^c

^aTSI France, Europarc, Bât. D., 13453 Marseille Cedex 13, France.

^bTSI GmbH, Neuköllner Str. 4, 52068 Aachen, Germany.

^cTSI Instruments Ltd., 1, Beach Road West, Portishead, Bristol, BS20 7HR, Great Britain.

Keywords: Nucleation; Ultrafines; Water-based condensation particle counter; Aerosol instrumentation

1. Introduction

Atmospheric nucleation is a process of environmental importance. It has both a direct and an indirect effect on the climate influencing the albedo and leading to optical extinction. The direct effect is due to the presence of newly formed particles and their interaction with sun light while the indirect effect is caused by the particles acting as cloud condensation nuclei. Additionally, newly generated nucleation particles in the nanometer range are said to have adverse effects on human health as they deeply penetrate into the lung where a fraction of them is deposited. The measurement of such nanoparticles generated by nucleation is a measurement challenge for conventional aerosol instruments. We describe a newly developed ultrafine water-based condensation particle counter (UWCPC), the TSI 3786, that is well suited for such measurements by extending the range of ultrafine particle detection techniques. We evaluated the performance of the instrument in the laboratory and describe its use in two experiments.

2. Atmospheric Nucleation

Nucleation is the formation of new, secondary particles from the gas phase. Nucleation has been frequently observed in the atmosphere. A review of observations published by Kulmala *et al.* (2004) lists more than 100 publications where nucleation has been observed since 1990. Nucleation has been observed almost everywhere, from clean remote environments to rural and polluted continental environments but also in exhaust emissions. Nucleation mechanisms include homogeneous condensation by both homomolecular and heteromolecular nucleation as well as heterogeneous condensation by homo/heteromolecular nucleation (Kulmala 2003). A special case is the so-called ion-induced or ion-mediated nucleation, when water condenses on an ion. The measurement of atmospheric nucleation has always been a measurement challenge for aerosol instruments. Until very recently nucleation has been experimentally observed only from 3 nm on with no information what happened below that size. Ideally, a measurement range from below 3 nm up to 30 nm needs to be covered to observe the formation and growth of nucleation mode particles. Also a wide concentration range is necessary for the instrument to being able to detect nanoparticles in clean environments, e.g. on mountaintop observatories, as well as high concentration nucleation bursts, e.g. at coastal locations.

3. Instrumentation to observe nucleation

Condensation particle counters (CPCs) are used to measure the number concentration of nucleation particles. Until recently the ultrafine condensation particle counter (UCPC) developed by Stolzenburg and McMurry (1991) and subsequently commercialized by TSI (model 3025) was the only commercial CPC that could detect particles as small as 3 nm (Sem, 2002). In addition, the TSI 3025A was used as part of electrical mobility spectrometers such as the scanning mobility particle sizer (SMPSTM) to measure the size distribution of nucleation particles. However, its low aerosol flow rate of 30 cm³/min affected the

counting statistics for clean atmospheric concentrations and its performance as a detector after a differential mobility analyzer (DMA). Recently a new ultrafine water-based CPC (UWCPC), the TSI 3786, was developed to improve on the performance of the 3025A and add several state-of-the-art features.

In operation the UWCPC draws in the aerosol sample to count the number of particles. The aerosol enters the sample inlet and immediately half of the 600 cm³/min inlet flow is extracted, filtered and then combined with the remaining sample flow as clean sheath air. The combined flow enters a region surrounded with wetted media. The UWCPC utilizes a new patented technology (Hering *et al.*, 2005) that allows water to be used as the working fluid without the requirement of mixing or adiabatic expansion techniques. A single wick, comprised of hydrophilic porous media, lines the inner walls of the conditioner and growth tube. In the conditioner the aerosol stream is saturated to near 100% RH with water vapor and is temperature equilibrated. In the subsequent growth section the walls are heated to provide the warm, wetted walls required for water condensational growth. The high diffusivity of water vapor allows the vapor to reach the center of the sample stream at a faster rate than the thermal diffusivity of the vapor can equilibrate to the higher temperatures near the walls. This results in a supersaturated condition along the radius of the flow stream. The sheath-air-flow design is used to keep the aerosol sample flow in the center of the growth tube where supersaturation is the highest. Particles in the flow stream act as nuclei for condensation and water continues to condense on the particles as it passes up the growth tube. The enlarged particles are then passed through a viewing volume illuminated by a laser. A silicon photodetector is used to detect light scattered from the particles (TSI Inc., 2005).

The new sheath-air-flow design allowed raising the detected aerosol flow to 300 cm³/min. This improvement results in ten times better counting statistics particularly at low, atmospheric conditions. It also improves the use after a DMA to measure high-resolution particle size distributions. In addition, the sheath-air-flow design produces a sharp counting efficiency curve by exposing particles to the highest level of supersaturation at the centerline of the condenser. The instrument's smallest-particle-size detection limit was lowered. Several new features were added including continuous live-time coincidence correction up to 100,000 particles/cm³, a removable single wick for easy maintenance, USB port for instrument control and data transfer, and ethernet capability. The UWCPC also offers a high data rate of 10 readings/sec and fast response to a concentration step change making it suitable to measure dynamic nucleation events. When used as a detector in the nano-SMPS the UWCPC offers high size resolution down to 2.5 nm with 64 channels resolution below 20 nm.

4. Instrument evaluation in the laboratory

We characterized the UWCPC for a number of key parameters such as its counting efficiency curve, smallest-particle-size detection limit, and response time to a concentration step change. We made measurements for the counting efficiency and smallest-particle-size detection limit characterization with outdoor ambient air and residue particles from ammonium acetate buffer. The ammonium acetate particles were generated by an electrospray aerosol generator 3480 and subsequently size selected by an electrostatic classifier with a nano-DMA 3085. The monodisperse aerosol from the nano-DMA outlet was mixed with HEPA-filtered air. A flow splitter was used to run a concentration reference and the UWCPC in parallel with the classified test aerosol. We used a UCPC 3025A as the reference initially due to electrometer noise issues at low concentrations. Down to about 5 nm both the UWCPC and the 3025A gave similar results. Below that size the UWCPC detected significantly more particles than the 3025A. For the smallest particle detection measurements, the UWCPC was compared with a custom WCPC which offered 100% detection efficiency for particles down to about 1.5 nm. The counting efficiency curve we determined shows a very steep slope. The particle size where the UWCPC has 50% counting efficiency (D_{50}) was determined to be 2.5 nm, making it the most sensitive ultrafine particle counter available. In addition we found that it still detected about 30% of the 2 nm particles. We also performed concentration step response tests to determine the UWCPC's response time for rapid changes. The 3786 showed a very fast response of < 2 seconds to 95% in response to the step change (T_{95}) for both increasing and decreasing concentrations.

5. Experiments

5.1. Measurements at nucleation flow tube at IfT Leipzig

In early 2005 we made laboratory experiments to investigate the rapid formation of new particles at near-atmospheric conditions at the Leibniz Institute for Tropospheric Research (IfT) in Leipzig, Germany. We used the UWCPC and a nano-SMPS at IfT's flow tube. In the flow tube H_2SO_4 particles can be produced in situ through reaction of OH radicals with SO_2 . Newly formed particles are observed for H_2SO_4 concentrations above 7×10^6 molecules/cm³. The nucleation rate is estimated to be 0.3 to 0.4 particles/cm³ per second at atmospheric H_2SO_4 concentration levels (Berndt *et al.*, 2005). Integral measurements of the freshly formed H_2SO_4 particles with UWCPC and UCPC 3025A in parallel showed a very similar response down to concentrations of 20 particles/cm³. Below that concentration the 3025A was no longer able to make meaningful measurements. The UWCPC with its 10 times higher detected aerosol flow, however, measured reproducibly down to concentrations as low as 2 particles/cm³. With the UWCPC we were able to measure the number of freshly generated particles down to H_2SO_4 concentrations of 1×10^7 molecules/cm³, which is close to the threshold at which new particle formation has been observed. In addition to measurements with the CPCs stand-alone we also used the UWCPC in a nano-SMPS to determine the size distribution of the freshly produced particles. Due to the low aerosol flow in the 3025A this has not been possible before at the very low concentrations after a DMA. Even with the UWCPC we measured less than 50 raw counts over one hour but were able to determine the nucleation particle size distribution. The mode of the distribution measured with the UWCPC in the nano-SMPS was found to be 2.64 nm, thus below the 3025A's smallest-particle-size detection limit.

5.2. Nucleation event at mountaintop observatory of Mt. Jungfraujoeh

We participated in field measurements as part of the Cloud and Aerosol Characterization Experiments (CLACE-4) campaign in March 2005. The campaign goals were to investigate the chemical composition of aerosol particles and their interaction with clouds. A special focus was new particle formation mechanisms by homogenous nucleation. The campaign site was the Sphinx laboratory at the high Alpine research station on Mt. Jungfraujoeh in Switzerland. The laboratory is located at 3,580 meters above sea level. Ambient conditions were outdoor air temperatures of -20°C and air pressures of 640 to 650 mbar on average. One of the UWCPC's benefits under these conditions is that it measures the inlet absolute pressure to make a continuous compensation of inlet and sheath flows. Prior to the measurements we matched the UWCPC's absolute pressure sensor to the high-precision pressure measurement of the Sphinx laboratory by a scale factor that can be sent by terminal command to the UWCPC. Initially we observed very clean atmosphere over many hours. The total number concentration of the clean background aerosol measured by the UWCPC was very low with typically only a few hundred particles/cm³. During nucleation events the concentration increased by a factor of four, which is still a low concentration for conventional electrical mobility spectrometers. An SMPS equipped with a long DMA and a 3025A was used outdoors in parallel with a nano-SMPS configured with the 3786 UWCPC. Although the conventional SMPS showed a very similar size distribution, only the nano-SMPS with the UWCPC was able to measure a smooth distribution with good counting statistics (Verheggen *et al.*, 2005). The nano-SMPS detected the formation and growth of the nucleation particles and showed a stable peak at 13 nm for several hours of measurements. The nucleation events lasted for up to 9 hours before the concentration dropped back to clean background levels with concentrations below 300 particles/cm³.

6. Summary

A new ultrafine water-based condensation particle counter, the model 3786, has been tested under laboratory and experimental conditions. The instrument uses water as its working fluid, which is odor-free and has no cross sensitivity with measurements of gaseous compounds. The UWCPC has a detected aerosol flow of 300 cm³/min which results in good counting statistics even at very low concentrations. The 3786's detected flow is ten times higher than in the UCPC 3025A, making the UWCPC ideally suited for nucleation measurements at clean atmospheres. Our laboratory performance evaluation has shown that the 3786 has a steep counting efficiency curve and a 50% counting efficiency at 2.5 nm. The UWCPC demonstrated a fast response to rapid changes in aerosol concentration ($T_{95} < 2$ seconds). The instrument also worked reliably during two experiments. Our measurements at IfT's nucleation flow tube showed that the UWCPC can make meaningful measurements down to the threshold at which formation of particles from H₂SO₄ has been observed. The field measurements on Mt. Jungfrauoch's mountaintop observatory demonstrated that the UWCPC is useful as detector in the nano-SMPS to measure low concentration nucleation events with good counting statistics.

Acknowledgements

The authors would like to thank Dr. Bart Verheggen and Dr. Ernest Weingartner (Paul Scherrer Institute, LAC, Villigen) for the opportunity to measure on Mt. Jungfrauoch during CLACE-4 and Dr. Torsten Berndt for the joint measurements at IfT Leipzig. We are also grateful to Dr. Wei Liu at TSI Incorporated who carried out most of the UWCPC performance tests.

References

- Berndt, T., Böge, O., Stratmann, F., Heintzenberg, J. and Kulmala, M. (2005) Rapid formation of sulfuric acid particles at near-atmospheric conditions. *Science*, 307, pp. 698.
- Hering, S.V., Stolzenburg, M.R., Quant, F.R., Oberreit, D.R., and Keady P.B. (2005) A Laminar-Flow, Water-Based Condensation Particle Counter (WCPC). *Aerosol Sci. Technol.* **39**, pp. 659–672.
- Kulmala, M. (2003) How Particles Nucleate and Grow. *Science*, **302**: pp. 1000-1001.
- Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P.H. (2004) Formation and growth rates of ultrafine atmospheric particles: a review of observations. *J. Aerosol Sci.* **35**: pp. 143-176.
- Sem, G.J. (2002) Design and performance characteristics of three continuous-flow condensation particle counters: a summary. *Atmospheric Research* **62**: pp. 267-294.
- Stolzenburg, M.R. and McMurry, P.H. (1991) An ultrafine aerosol condensation nucleus counter. *Aerosol Sci. Technol.* **14**, pp. 48-65.
- TSI, Inc. (2005). Model 3786 Ultrafine Water-based Condensation Particle Counter Operation and Service Manual. P/N 1930072, Revision A (January 2005).
- Verheggen, B., Cozic, J., Weingartner, E., Mertes, S., Flynn, M., Connolly, P., Bower, K.N., Gallagher, M. and Baltensperger, U. (2005). Nucleation and activation of aerosol particles during CLACE Campaigns (Jungfrauoch, 3580 metres a.s.l., Switzerland). *Abstracts of the European Aerosol Conference 2005*, Ghent-Belgium.