WP3- NA3: In-situ chemical, physical and optical properties of aerosols Deliverable D3.8: Intercomparison workshop for nano-MSP and AIS for the nucleation mode range

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Definition: Instead of MSP (Mobility SPectrometer), we will use the terminology "Mobility Particle Size Spectrometers (MPSS)" in future.

Within Task 3.1,

1. nano-mobility particle size spectrometers (nano-MPSS) and ion spectrometers (AIS) has to be characterized in terms of losses
2. a modified method to calculate particle losses has to be developed based on the method of the "equivalent length"
3. a measurement protocol will be developed and
4. the overlap between AIS and MPSS has to be quantitatively improved by developing a correction function for the inversion algorithm

Therefore, an expert-user instrumental workshop for nucleation mode particle measurements was held from 24 September to 7 October 2012 at the University of Helsinki, Finland. The overall goal of this workshop was to initiate the work within ACTRIS 1) to standardize the nano-MPSS and AIS measurements, and 2) write a protocol for nano-MPSS and AIS measurements. The main participants for the workshop were partners UHEL (University of Helsinki) and TROPOS (Leibniz Institute for Tropospheric Research).

The starting point for our workshop is work done by Wiedensohler et al. (2012), who wrote and published in *Atmospheric Chemistry and Physics* standardization for atmospheric particle number size distribution measurements (http://www.atmos-meas-tech.net/5/657/2012/amt-5-657-2012.pdf). Their work sums up the results from several intercomparison workshops conducted within the European infrastructure project EUSAAR (European Supersites for Atmospheric Aerosol Research) and ACTRIS to determine present uncertainties especially of custom-built nano-MPSSs. Under laboratory conditions, the particle number size distributions from 20 to 200 nm determined by MPSS of different design are within an uncertainty range of around ±10% after correcting internal particle losses, while below this size range, in nucleation mode range, the discrepancies increased.

We focus especially on the nucleation mode range. Secondary formation of nucleation mode particles in the atmosphere is a globally important source of aerosol loading, and it has important influence on Earth's climate. Thus, we aim to harmonize the measurements of these particles, which is crucial for data interpretation. During the workshop, we aimed to ensure the consistency of measured particle number size distributions and to perform intercomparison using ambient/generated aerosol in the nucleation mode range with particles smaller than 25 nm. The consistency of particle number size distribution measurements of a UHEL nano-MPSS and the ACTRIS reference MPSS (TROPOS) within the nucleation mode size range (<25 nm) was verified with artificial, polydisperse silver particles.

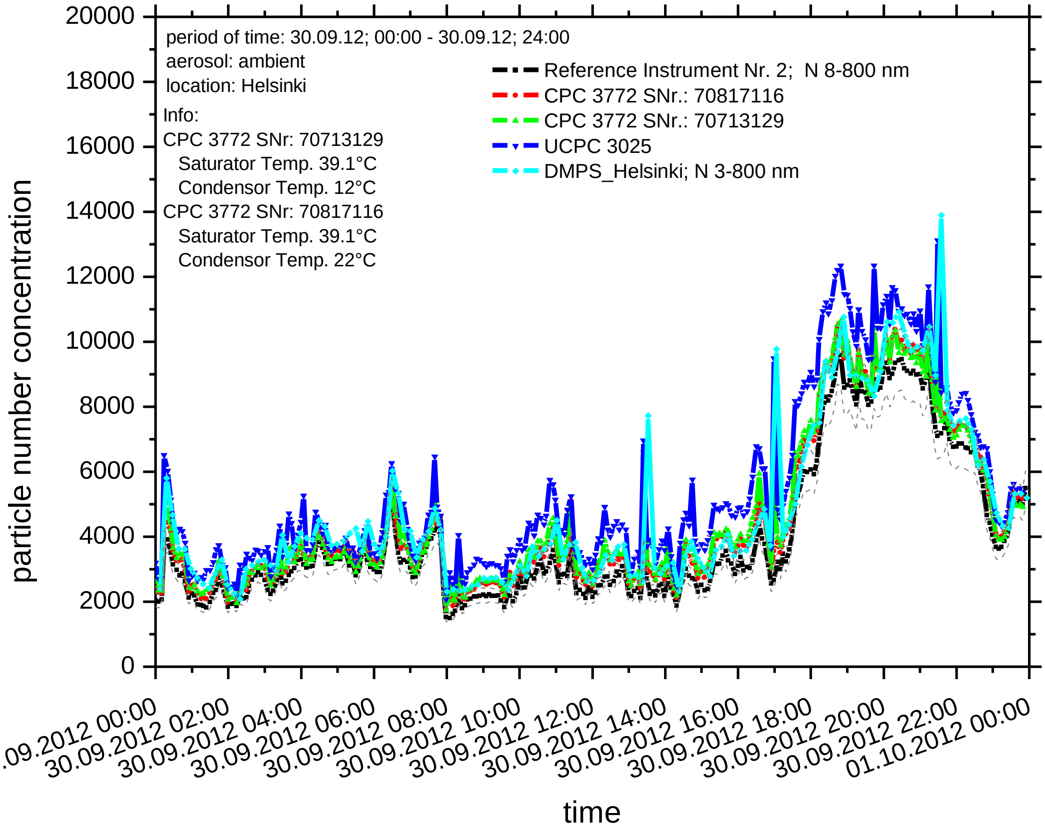

Figure 1. Total concentration comparison between nano-MPSS (DMPS-Helsinki), standard MPSS (Reference Instrument), several nano-Condensation Particle Counters (CPC 3025 and 3772's) when ambient sample was measured 24 hours on 30.9.2012 in Helsinki.

In Fig. 1, the total concentration measured with different instruments is compared and to test the reliability for measurement protocol which is the third aim within task 3.1. The difference was the highest when a peak appeared in the number concentration which indicated local pollution from traffic. Typically, these particles are slightly larger than nucleation mode particles. Clearly, the discrepancy between the instruments increased within the nucleation mode size range, which is consistent with earlier results and demonstrates the urgent need to organize this workshop.

UHEL has been working in the past to harmonize the nucleation mode measurements. A measurement protocol for nucleation mode particles was published in *Nature Protocols* by Kulmala et al. (2012, http://www.nature.com/nprot/journal/v7/n9/pdf/nprot.2012.091.pdf). They describe the present instrumentation, best practices and other tools used to investigate atmospheric nucleation. The key instruments comprise devices capable of measuring the number concentration of the formed nanoparticles and their size, such as air ion spectrometers, and mobility particle size spectrometers. The work to measure nucleation mode particles as reliably as possible is still continuing with the ACTRIS project.

For this expert workshop, UHEL build a nano-MPSS which was measuring specifically the nucleation mode range (3-45 nm) aerosol particles. The nano-MPSS was combined with a standard MPSS measuring from 20 to 820 nm. Both of the instruments were calibrated prior to the workshop. UHEL tested and verified the operation of Neutral cluster and Air Ion Spectrometer (NAIS, 2-40 nm). Several nano-Condensation Particle Counters (nano-CPCs, >3 nm) were calibrated to be used as reference instruments for total particle number measurements. TROPOS prepared and calibrated the ACTRIS-reference MPSS, which measures in the size range from 8-800 nm.

The consistency of particle number size distribution measurements of UHEL and TROPOS instruments at sizes 80, 100, 200 and 400 nm was verified using artificial, monodisperse, test particles to confirm to consistence with the earlier studies. The measured particle number size distribution of all instruments agreed well in these four size ranges, as the observed and theoretical value agreed within the error limits (see Fig. Table 1). The deviation of the particle sized measured by the standard MPSS (STD-MPSS) is too high compared to the reference, which can be corrected by calibrating the sheath flow of the STD-MPSS, as suggested by Wiedensohler et al. (2012), against the Latex (PSL) particles.

PSL (nm)	REF-2 (nm)	STD-MPSS (nm)	Nano-MPSS (nm)
80±4	82.0	77.6	78.9
97 ±3	99.1	95.0	96.6
200±6	200.1	190.0	197.6
404±4	406.6	384	-

Table 1. Ensure the consistency of size distribution measurements of workshop UHEL and TROPOS instruments at sizes 80, 100, 200 and 400 nm with PSL particles.

In nucleation mode size range, this was done by using artificial, polydisperse silver particles. We observed some discrepancy between the instruments within the nucleation mode size range. The intercomparison based on data of the ambient aerosol was performed with all different available (TROPOS-reference MPSS, UHEL nano-MPSS, UHEL MPSS, NAIS, nano-CPCs). The aim was to compare the measured total number concentrations. In addition, the ambient aerosol sample was mixed with polydisperse nucleation mode size silver particles to test how well the instruments agree when nucleation mode is present (see Appendix Fig. A2).

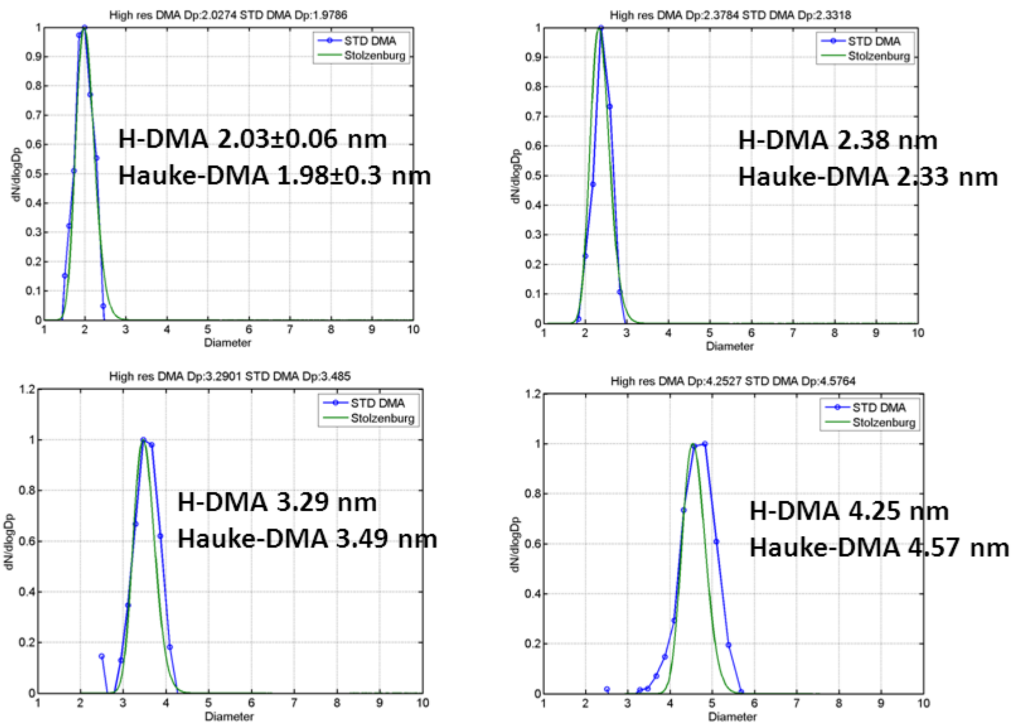

Figure 2. Calibration of the anano-MPSS (Hauke-DMA) against the high resolution H-DMA in nucleation mode range for four generated silver particle sizes (blue line measured and green theoretical size).

UHEL Nano-MPSS was calibrated with a High resolution Differential Mobility Analyser (H-DMA) to measure the transfer function width and total loss term in size range 2-4 nm (see Appendix Fig. A1). Example of the results is presented in Fig. 2. The measured particle number size distribution for generated silver particles matched very well with the theoretical, suspected size. The Nano-MPSS was measuring nucleation mode particle size very accurately.

UHEL together with University of Tartu started to make the first version of the combined inversion algorithm of the NAIS-nano-MPSS to merge the MSP and NAIS data (Manninen et al., 2012). Fig. 3 shows the first version of the merged particle number size distribution measured with MPSS and ion spectrometers without any corrections or modifications. The advantage of the NAIS is that it can measure particles as small as 2 nm in diameter, whereas the disadvantages include possible turbulence in the analyzer and under-estimation of multiply charged particles. In the larger particle sizes (>15-20 nm), the concentrations are overestimated due to multiply charging of the particles, which NAIS inversion is not able to take into account due to the lack of a pre-impactor. This disadvantage is very clear in Fig. 3 in left panel as there is a clear gap in the merged number size distribution at 20 nm where the spectras as merged together (without any fitting). The NAIS observes particles at too small sizes because of their multiple charges. During secondary formation of new particles the merging is much better as the mode of large, longtransported, aerosol particles doesn't exist.

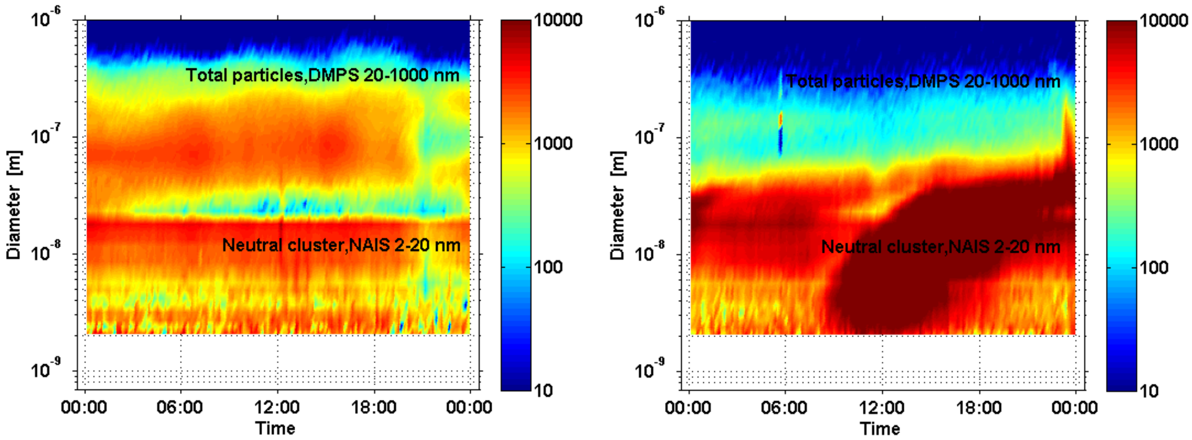

Figure 3. Merging MPSS and ion spectormeter spectras: Particle size distribution measured with the NAIS in 2–20 nm and with the MPSS in 20–1000 nm on April 4 (left) and April 19, 2011 in Hyytiälä.

To reach the fourth aim of the task 3.1 - the overlap between AIS and MPSS has to be quantitatively improved by developing a correction function for the inversion algorithm – we will continue working with the combined inversion algorithm of the NAIS-nano-MPSS to merge the MPSS and NAIS data. Using the MPSS data as background information for the NAIS inversion, we will take into account the multiply charging and improve the fit.

The losses inside the instruments were measured for the nano-MPSS and standard-MPSS, whereas for the NAIS they were not measured within this workshop. Therefore, to fulfil aims of characterizing both instruments, in terms of losses and describing this with "equivalent length", needs continuation of laboratory work.

Based on the good results and feedback from this workshop, we will organize another expert workshop for nucleation mode particle measurements in Helsinki. The workshop is already announced at the ACTRIS intranet:
The 2nd Nano mobility particle size spectrometer and NAIS scientific intercomparison workshop will be organized by Tuukka Petäjä at the University of Helsinki, Finland, from Oct 14-25, 2013, as decided during the WP3 meeting in Leipzig in October 2012.

References

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Appendix A:

PARTICIPATION ACTRIS WP3,D3.8 WORKSHOP
24.9.-7.10.2013 University of Helsinki, Finland

#	Name	surname	institution	country	email
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Appendix B.

AGENDA ACTRIS WP3,D3.8 WORKSHOP
24.9.-7.10.2013 University of Helsinki, Finland

Program for the workshop:

Goals of the workshop:
1) to ensure the consistency of size distribution measurements of UHEL and TROPOS instruments at sizes 80, 100 and 400 nm with PSL particles
2) to perform total loss term measurements in size range 10-40 nm (TROPOS) and 2-40 nm (UHEL)
3) to perform intercomparison based on data of the ambient aerosol (TROPOS-DMPS, UHEL DMPS, UHEL-UF, NAIS, total CPC)

for UHEL systems:

4) check of transfer function width with HDMA setup
5) check of HDMA and Hauke mobilities
6) to make the first version of the combined inversion algorithm of the NAIS- nano-MPSS

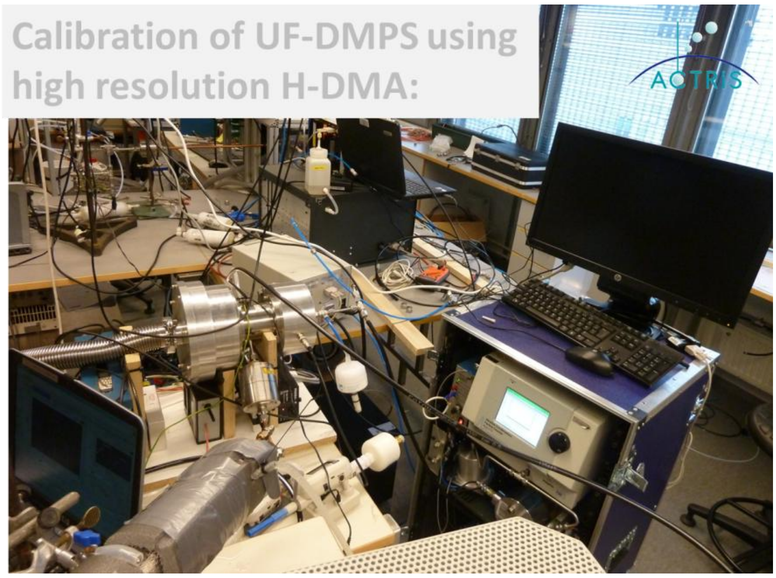
Tasks 1-2 first week, Task 3 over the weekend.

First week:

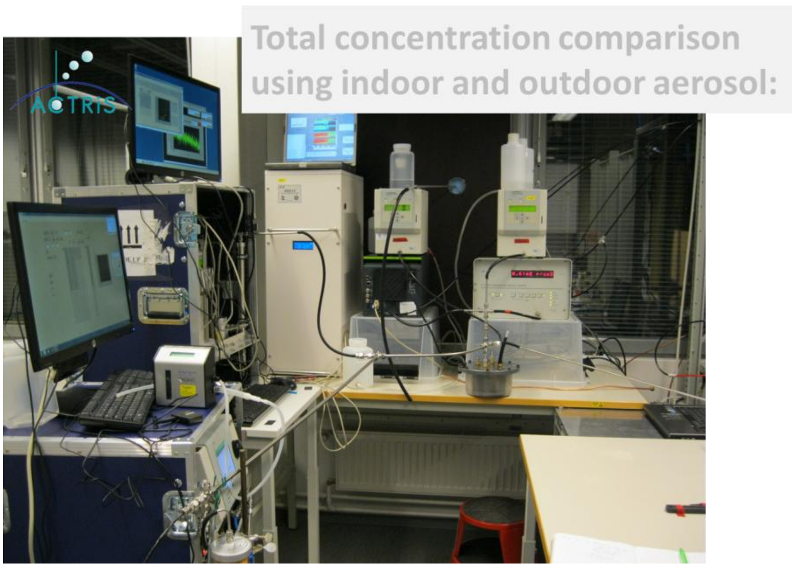
Monday 24.9.:
Arrival, instrument preparations/checks
Tuesday 25.9.:
Instruments checks, PSL measurements

Wednesday 26.9.:
PSL measurements continue
Thursday 27.9.:
PSL measurements continue,
Preperations for ambient aerosol measurements
Friday 28.9. – Saturday 29.9.:
Ambient aerosol measurements

Second week:
Open program for suggestions.



Appendix Fig A1: Workshop calibration instrumentation and set-up.



Appendix Fig A2: Workshop intercomparison instrumentation and set-up.