Size Distribution and Elemental Composition of Airborne Nanoparticles Measured On-Line by SMPS-ICPMS Coupling Technique

Adrian Hess[1,2], Adrian Wichser[1], Mohamed Tarik[3], Christian Ludwig[2,3]

[1] EMPA – Swiss Federal Laboratories for Material Science and Technology, CH-8600 Dübendorf, Switzerland.

[2] EPFL – Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

[3] PSI – Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland.

Corresponding author: adrian.hess@empa.ch

Introduction

Aerosol properties like size particle concentration and size distribution can be determined on-line by well-established measuring techniques. Besides there exist procedures and techniques for measuring size-resolved the chemical composition of aerosol particles, like electrostatic sampling followed by electron microscopy analysis, or size resolved sampling of particles in a cascade impactor and subsequent acid digestion and chemical analysis of the sampled size fractions.

However, these established techniques do not provide physical and chemical information at the same time, i.e. no traditional techniques providing on-line information on the size-resolved chemical composition of airborne particles are available.

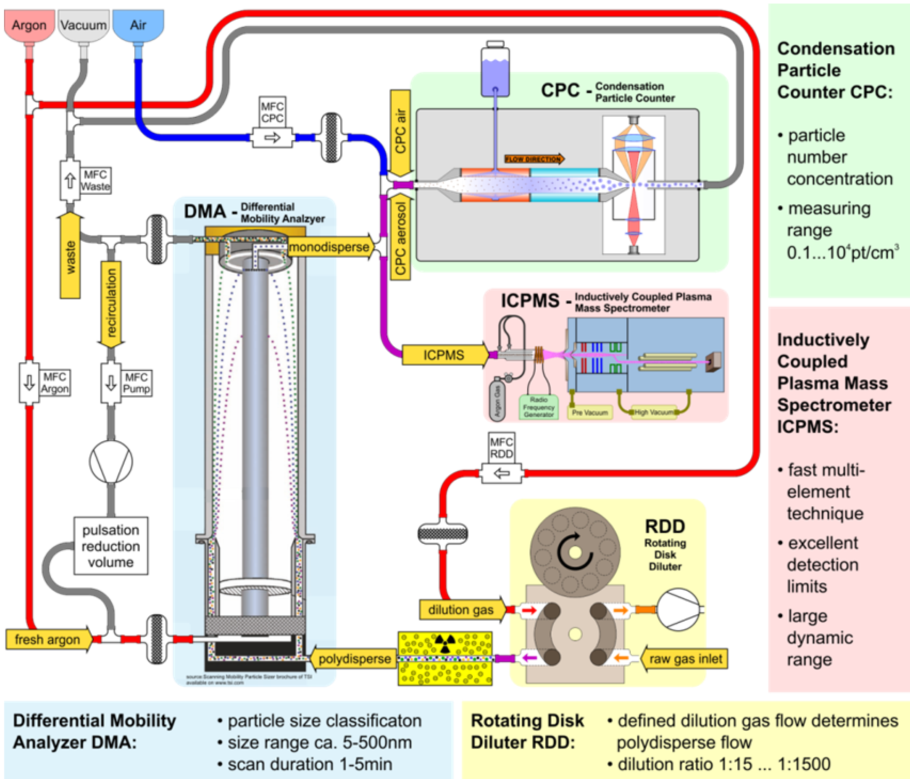


Fig. 1: Flow concept of SMPS-ICPMS

Scanning Mobility Particle Sizer (SMPS) is widely used for physical characterisation of aerosol particles in a range from about 5 to 500 nm. A common SMPS setup consists of a Differential Mobility Analyser (DMA) classifying airborne particles according to the mobility diameter, and a Condensation Particle Counter (CPC) determining the number concentration of the prior classified particles.

Inductively Coupled Plasma Mass Spectrometry (ICPMS) allows determining the elemental composition of analysed matter with excellent detection limits and a wide dynamic measuring range.

Coupling of SMPS and ICPMS allows achieving size and chemical information simultaneously. The expected full scan duration of a few minutes and the even shorter scan time for a narrower size range enables transient particle observation, and it opens the possibility to chemically characterise an aerosol in its original condition instead of size-fractionated particle sampling and subsequent off-line chemical analysis.

Flow Concept for SMPS-ICPMS Coupling

Due to the low oxygen tolerance of the inductively coupled argon plasma the size fractionated particles have to be carried by argon when entering into ICPMS. This means that a gas exchange has to be maintained, and the DMA is therefore operated using argon as sheath gas instead of air.

A Rotating Disk Diluter RDD was implemented to enable a proper control of the aerosol flow into the DMA. This device allows having a defined dilution gas flow where a certain amount of raw gas can be added, resulting in a controlled diluted aerosol flow. The RDD is operated using argon as dilution gas to minimise the air entry to the system.

The flow concept of the modified SMPS coupled to ICPMS is illustrated in Fig. 1.

SMPS Argon Operation

The argon operated SMPS was validated by measuring standard aerosols using either air or argon as sheath gases. These measurements were performed while two standard operated reference SMPS instruments were attached in parallel to the device under test. Standard PSL particles in air were used for these validation measurements. The resulting particle size distributions are shown in Fig. 2.

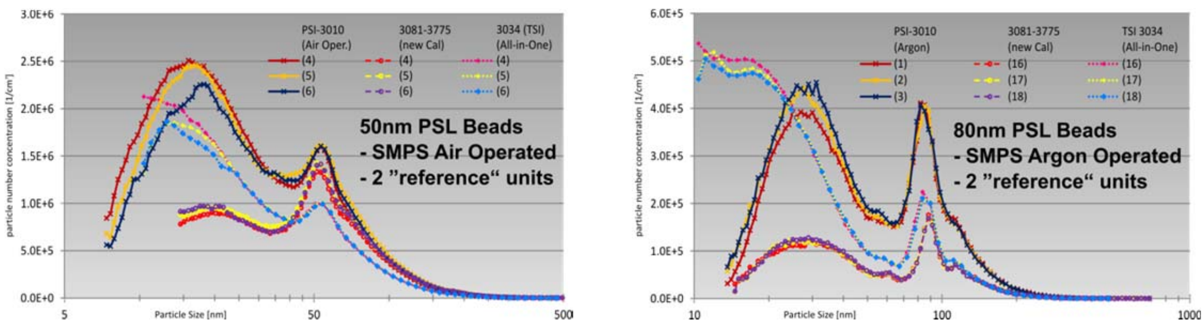


Fig. 2: Air (left) and argon (right) operated SMPS validation measurements; comparison to 2 reference instruments

The tested instrument is labelled as "PSI-3010". "3081-3775" and "TSI 3034" were standard operated SMPS systems used as reference devices. The size-related counting efficiencies seem to differ significantly between all compared SMPS instruments. However the reference peaks are correlated to the correct particle diameter by all instruments. The correlation of the size distributions measured by instrument under test to those of the reference instruments seems to be similar in argon as in air operation.

First Coupling Attempt

A suspension containing citrate covered silver nanoparticles in water with a mean diameter of 70 nm was used to generate a sample aerosol. The suspension was dispersed into air. This aerosol was then dried in a thermo denuder, resulting in a dry aerosol containing airborne silver nanoparticles. The generation of this aerosol is illustrated in Fig. 3.

This aerosol was supplied to the non-calibrated RDD where it was diluted with argon by a factor of about 20, before being introduced to the DMA. SMPS scans were recorded while ICPMS was measuring the silver atom masses Ag107 and Ag 109 continuously.

Some of the data obtained in terms of the first coupling attempts are shown in Fig. 4. The upper plot shows the number weighted particle size distribution determined by the argon operated SMPS when the silver aerosol described above was supplied to the RDD at the SMPS-ICPMS inlet. The mean diameter of this measured distribution lies between 30 and 40 nm.

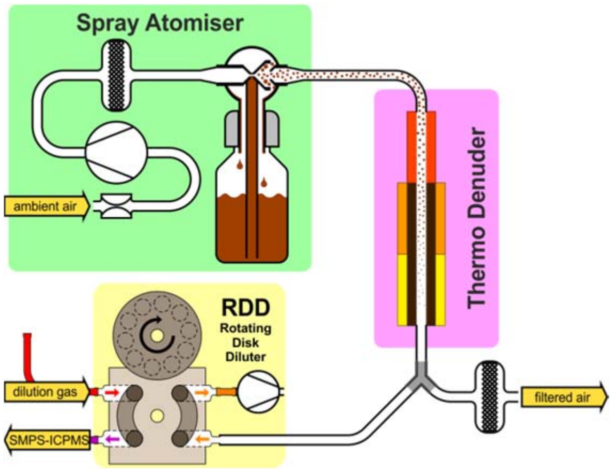


Fig. 3: Test aerosol generation

The total particle volume weighted size distribution shown in the centre of Fig. 4 is roughly estimated assuming spherical particles. The mode of this curve lies between 80 and 90 nm which is closer to the expected 70 nm than that of the number weighed plot.

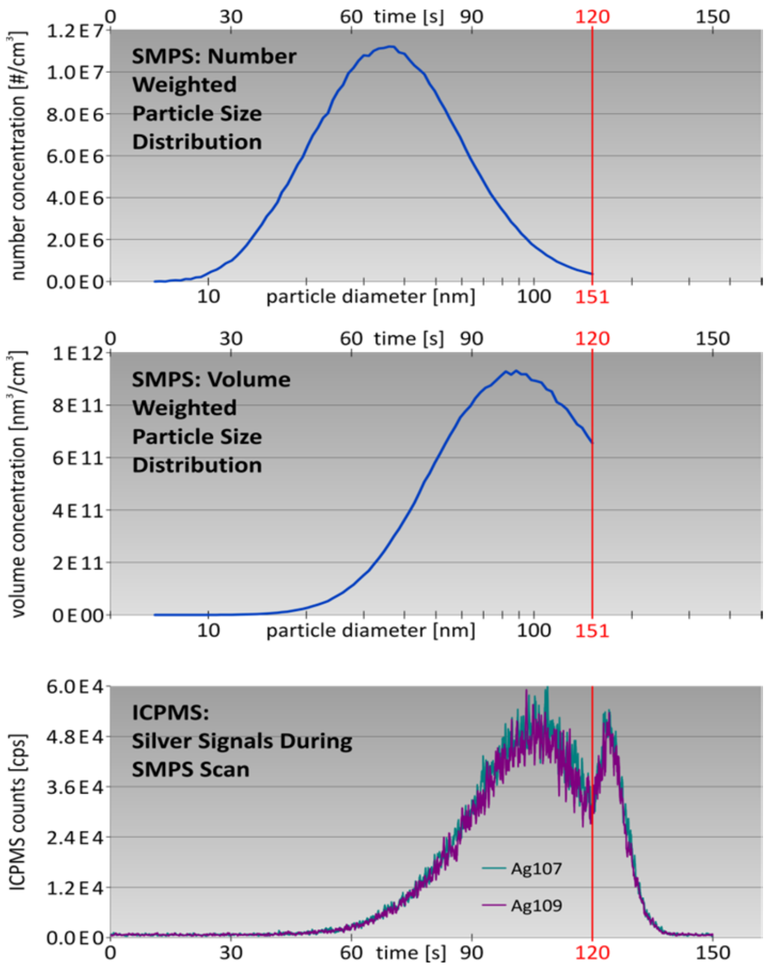


Fig. 4: SMPS size distributions and simultaneously measured ICPMS signal

The curve at the bottom shows the ICPMS silver signals, i.e. the the atomic masses 107 and 109. The minima of both signals at 120 s allows to synchronise the ICPMS signals to the SMPS scan since this minimum indicates when the DMA voltage changed from scanning up- to downwards. This synchronised mass signal appears to correlate fairly well to the volume weighted SMPS curve.

Outlook

In the next phase the coupled setup will be optimised and characterised in detail. This includes coupling the SMPS to a modern state-of-the-art ICPMS instrument, determining appropriate SMPS and ICPMS operation modes, finding optimal operation parameters, and assessing measures to keep the consumption of the relatively expensive argon on a moderate level.

The novel setup will be validated using standardised aerosols containing nanoparticles of different compositions and size distributions and applying established off-line particle characterisation techniques like size fractionated sampling and subsequent ICPMS analysis or single-particle precipitation and electron microscopy investigations.

In the last project phase SMPS-ICPMS will be applied in concrete research projects where airborne engineered nanoparticles released by consumer spray products and combustion generated nanoparticles emitted by waste incineration processes have to be physically and chemically characterised.

Size Distribution and Elemental Composition of Airborne Nanoparticles Measured On-Line by SMPS-ICPMS Coupling Technique

Adrian Hess[1,2], Adrian Wichser[1], Mohamed Tarik[3], Christian Ludwig[2,3]

[1] EMPA – Materials Science and Technology – Dübendorf, Switzerland
[2] EPFL – Ecole Polytechnique Fédérale de Lausanne – Lausanne, Switzerland
[3] PSI – Paul Scherrer Institute – Villigen, Switzerland

Introduction

Monitoring of Airborne Nanoparticles:

Scanning **M**obility **P**article **S**izer SMPS:
- Particle number concentration
- Particle size distribution

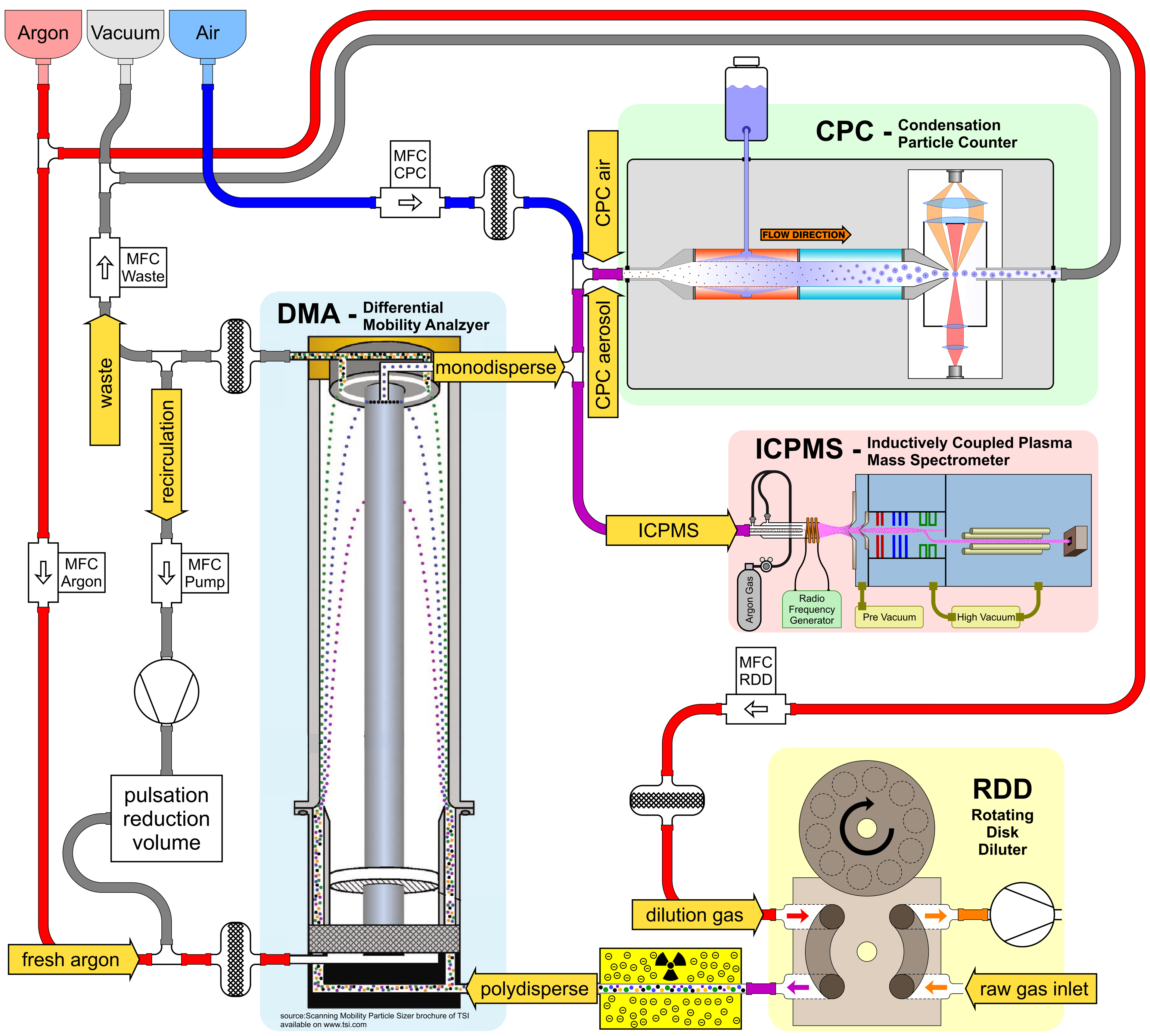
Inductively **C**oupled **P**lasma **M**ass **S**pectrometry ICPMS:
- Off-line chemical (elemental) composition

Novel Coupling of SMPS and ICPMS
- Simultaneous size / chemical information
- Scan durations ~ several minutes

Benefits of SMPS-ICPMS Coupling
- ☺ Quasi on-line technique
- ☺ Direct monitoring of dynamic aerosol properties / behaviour
- ☺ Chemical analysis without prior sampling and sample storage / handling

Challenges / Limitations
- ⚠ Low oxygen tolerance of Ar plasma
- → SMPS operated using Ar instead of air
- ⚠ Lower dielectric strength of Ar than air
- → Limited high voltage, i.e. particle size range
- ⚠ Sample introduction to plasma
- → Rotating disk diluter to control inlet flow
- ⚠ Strong ICPMS background signal by gaseous air pollutants
- → (argon operated rotating disk diluter)

Flow Concept for SMPS-ICPMS Coupling



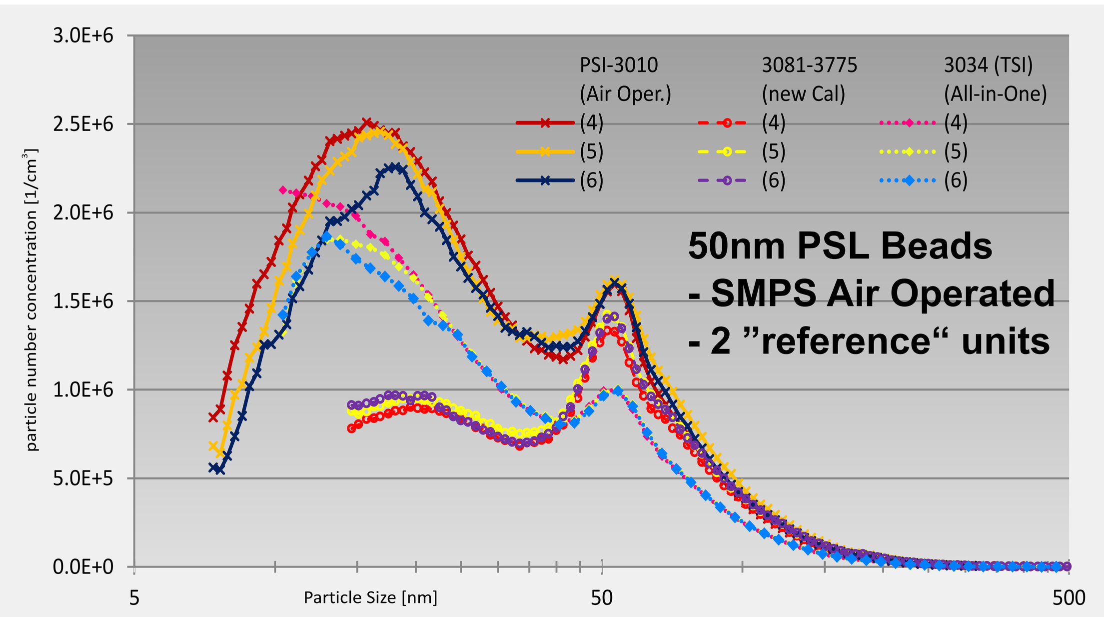
Condensation Particle Counter CPC:
- particle number concentration
- measuring range 0.1...10^4 pt/cm^3

Inductively Coupled Plasma Mass Spectrometer ICPMS:
- fast multi-element technique
- excellent detection limits
- large dynamic range

Differential Mobility Analyzer DMA:
- particle size classificaton
- size range ca. 5-500nm
- scan duration 1-5min

Rotating Disk Diluter RDD:
- defined dilution gas flow determines polydisperse flow
- dilution ratio 1:15 ... 1:1500

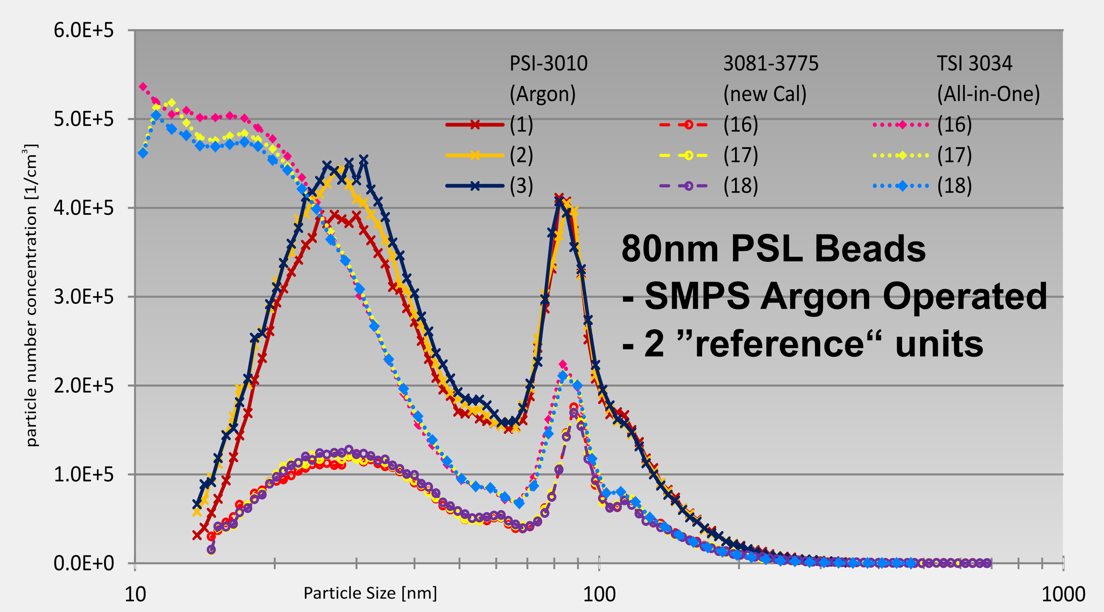
SMPS Argon Operation



Air and argon operated SMPS compared with 2 air operated "reference" devices

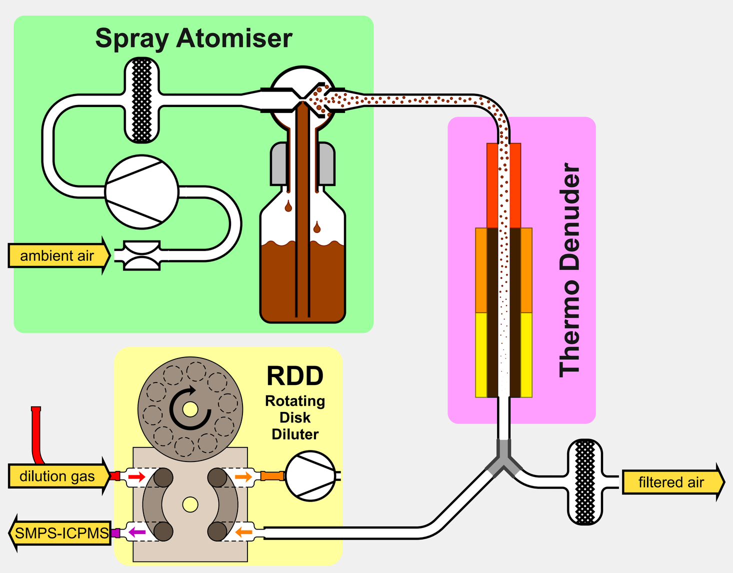
Strongly varying counting efficiencies at very small particle sizes but good size agreement at reference peak (50 resp. 80nm)

Very good Air-argon Correlation



Results of First Coupling Attempt

Suspension containing 70nm silver particles dispersed into air.

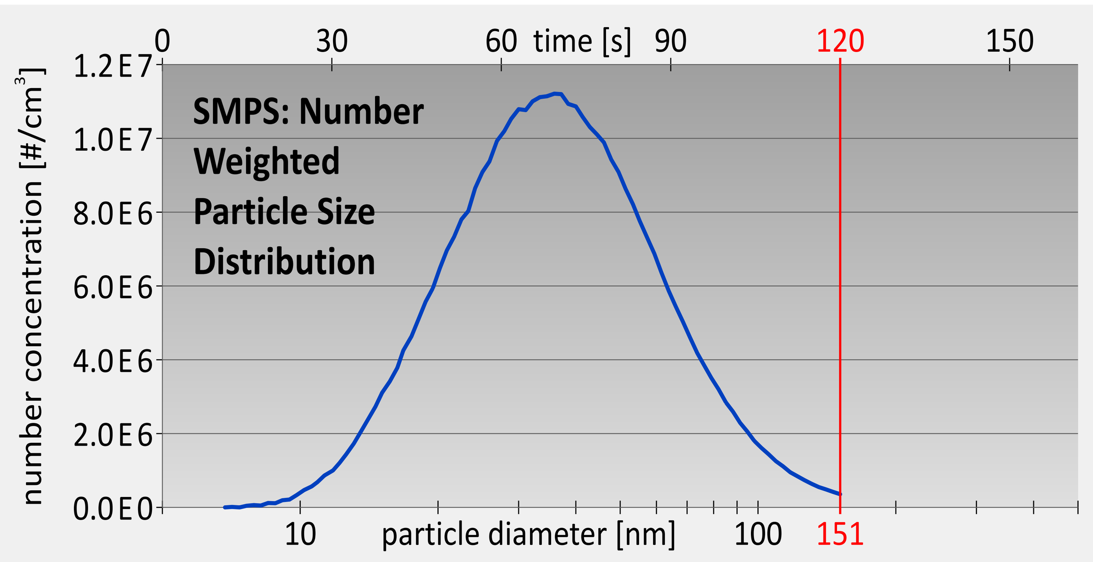


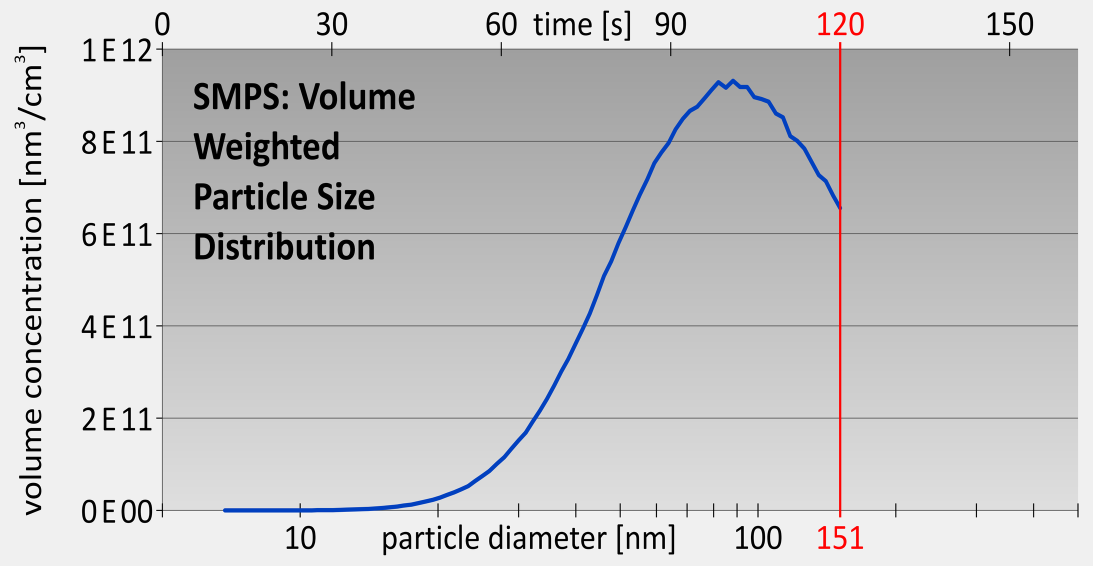
Aerosol dried by thermo denuder.

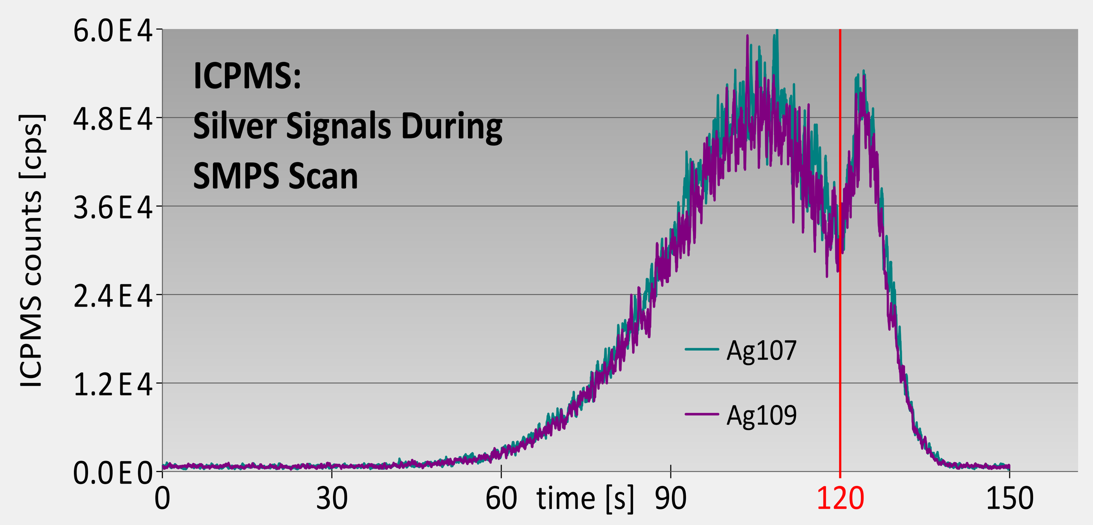
Ag 107 and Ag 109 masses measured by ICPMS.

No obvious correlation of number weighted size distribution to Ag signals since ICPMS signal is mass based.

Good correlation of volume weighted size distribution recorded by SMPS to real-time ICPMS signal on both Ag masses.







Acknowledgements

We are grateful to CCMX and R'Equip for financial support, and to our project collaborators PSI, FHNW, TSI GmbH, HeiQ Materials AG, Matter Aerosol AG, and NanoSys GmbH.

Contact: Adrian Hess - adrian.hess@empa.ch

presented at: 17th ETH Conference on Combustion Generated Nanoparticles, June 23rd-26th, ETH Zürich, Switzerland