On-Line SMPS-ICPMS Coupling for Simultaneous Analsysis of Nanoparticles Concerning Size Distribution and Elemental Composition

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Introduction

Scanning Mobility Particle Sizer (SMPS) is a widely established technique for on-line determination of particle size distribution and concentration in aerosols with temporal resolutions of a few minutes. Inductively Coupled Plasma Mass Spectrometry (ICPMS) is a chemical analysis technique providing information on the elemental composition of usually liquid (dissolved) samples. Chemical nanoparticle analysis is mostly done off-line, including a series of working steps, as particle sampling, storage, transport, preparation, and finally analysis. Alternatively, nanoparticles are on-line chemically characterised, e.g. by ICPMS, but without having size information.

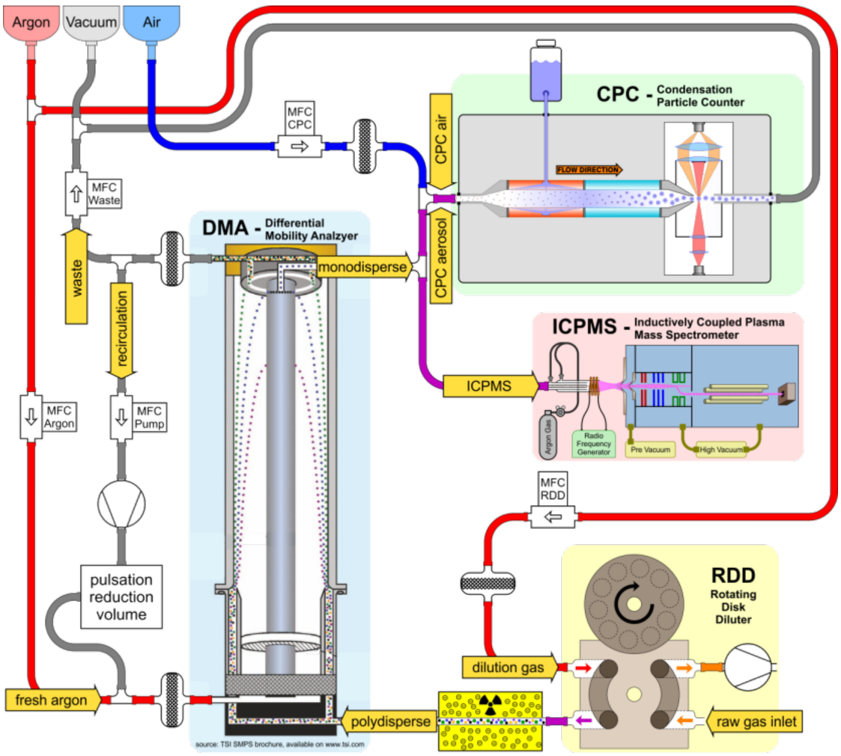

Fig. 1: Flow concept of SMPS-ICPMS

By coupling SMPS and ICPMS both information, i.e. particle size distribution and size resolved chemical composition, can be recorded at the same time. Therewith the time consuming and error-prone particle sampling and preparation procedure can be avoided. Besides, on-line chemical information with temporal resolutions similar to SMPS is available. Implementing a Rotating Disk Diluter as sampling interface enables in-line aerosol sampling, independent of a primary flow rate of the investigated aerosol. There are many applications for this hyphenated technique, examples are the assessment of consumer products containing engineered nanoparticles (ENP), research on metals in engine exhaust aerosols, or monitoring of waste incineration emissions.

Coupling Setup

The flow concept of the SMPS-ICPMS coupling setup is sketched in Fig. 1. The Differential Mobility Analyzer (DMA) serves to select one particle size fraction at a time. The Condensation Particle Counter (CPC) determines the number concentration of particles in this selected particle size fraction. SMPS and CPC are the core components of the standard operated SMPS.

ICPMS was added to this setup as a second particle detector, installed in parallel to the CPC. The argon plasma at the ICPMS inlet exhibits low air tolerance, meaning that nitrogen and oxygen content in the introduced sample should not exceed 10 %, better 5 %. Thus, the coupled SMPS is run using argon as sheath gas instead of originally air. In contrast to the CPC, ICPMS is not able to aspirate the aerosol flow needed for the measurement, but the sample has to be actively directed into the plasma. So the DMA sample outlet and therewith also sample inlet flows are no longer defined by the CPC inlet flow. Therefore a Rotating Disk Diluter (RDD) was implemented which allows precisely adjusting the dilution gas and therewith the diluted measuring aerosol flow being conducted to DMA.

A certain fraction of the classified aerosol at the DMA outlet is then absorbed by the CPC, while the remaining portion is introduced to the ICPMS plasma.

Measuring Arrangement

The measuring arrangement is illustrated in Fig. 2. A nanoparticle containing suspension is provided to a spray aerosol generator. The aerosol has to pass a diffusion aerosol drier where the water is removed from the nanoparticle containing spray droplets, resulting in dried particles, available for instrument characterisation. This dry aerosol is split into two fractions, absorbed by two separate RDD's. One of them is the argon operated sample interface of SMPS-ICPMS, the other is air operated and connected to a non-modified reference SMPS which has been added in order to validate the data from the modified and coupled SMPS.

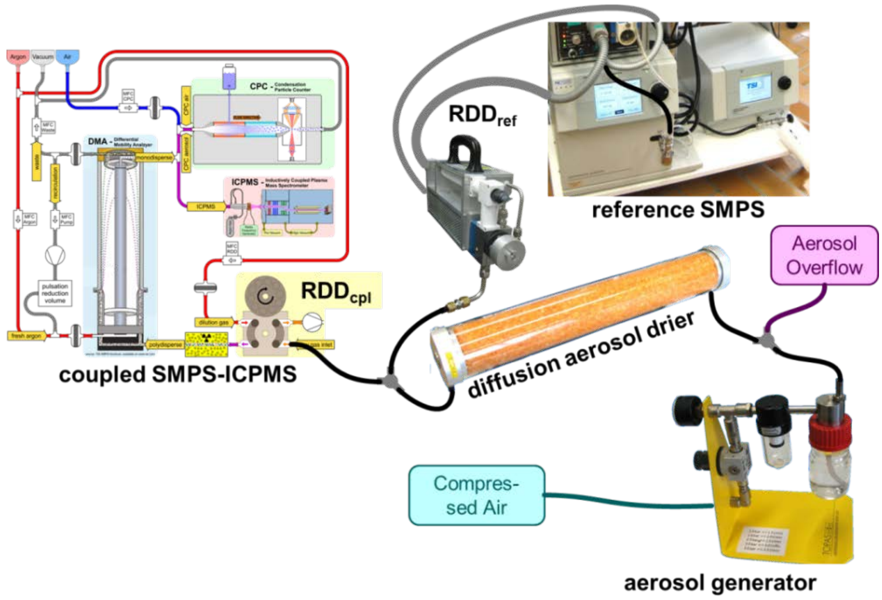

Fig. 2: Measurement arrangement including aerosol generator, diffusion drier, coupled SMPS-ICPMS, and reference SMPS instrumentation equipped with separate RDD

Measuring Results on Model Aerosol

Two aqueous suspensions containing smaller gold and larger silver nanoparticles with nominal diameters of about 20 nm and 80 nm were blended and introduced to the aerosol generator. Fig. 3 shows the data, resulting from measuring this aerosol with SMPS-ICPMS. The number corrected ICPMS intensities were calculated from the originally mass related signals and compared to the natively number based SMPS curve in the left graph. Vice versa, the volume weighted size distribution was calculated from the number weighted SMPS data and compared to the initially mass related ICPMS intensities in the right diagram.

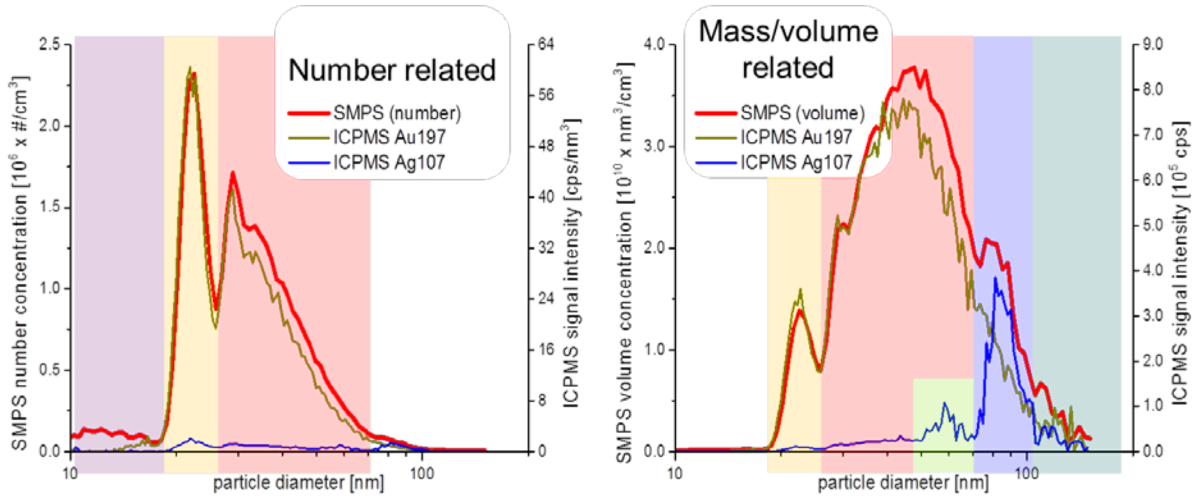

Fig. 3: Number (left) and mass/volume (right) weighted size distribution measured by SMPS, compared with size-resolved ICPMS intensities of m/z: 197 (gold) and m/z: 107 (silver)

The nominally 20 nm gold particles were recognised by the coupled SMPS-ICPMS. The wider distributed particles between 30 and 70 nm were also clearly identified as gold particles since the ICPMS gold curve follows very well the SMPS curve in this range. The SMPS curve features another peak between 80 and 90 nm, especially visible in the volume weighted diagram. Since the ICPMS gold curve does not follow this peak but the silver curve exhibits a peak at this particle diameter, this peak was found to represent the silver particle fraction. Therewith the SMPS-ICPMS coupling was able to clearly distinguish between the 20 nm gold and 80 nm silver particles.

Real Sample Analysis (Part of NanoSpray Project)

As a real sample, tin nanoparticles emitted by a dirt repellent consumer pump spray product were characterised. The spray bottle was placed in a glove box and 3 pump strokes were conducted. The left diagram in Fig. 4 shows the number weighted particle size distributions determined by SMPS. From these data, the volume weighted size distributions in the central graphics were calculated, assuming spherical particles.

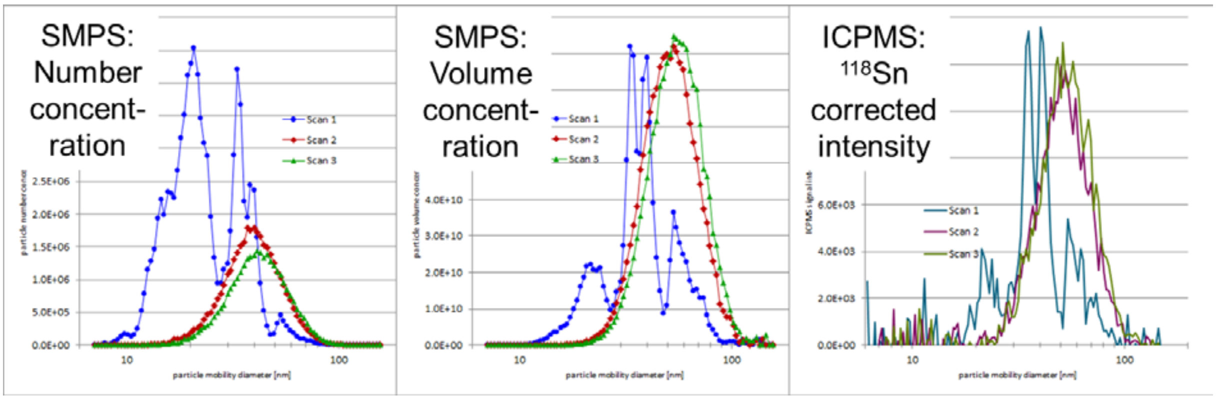

Fig. 4: SMPS-ICPMS data on tin particle containing real sample

The blue curves represent the first SMPS scan which was started immediately after the spray activation, the red and green curves originate from the second and third scans, started 3 and 6 minutes later. During the first scan, high number concentrations of small particles were measured and peaks at different particle diameters were detected. These number concentrations rapidly decreased and monomodal size distributions arose. The volume weighted size distribution was also moving towards larger particles and the multiple modes changed to a monomodal distribution, but the integrated volume concentration was not changing dramatically. Since the size resolved ICPMS ^{118}Sn intensities in the right diagram match very well to the volume weighted size distributions, it was clearly shown that the tin content in the particles remained unchanged and therewith these concentration and size distribution alterations were only caused by particle agglomeration, and not e.g. by particle loss and simultaneous particle growth by condensation of volatile matter in the atmosphere. The hyphenated technique could therewith proof its ability to dynamically observe nanoparticle behaviour, not only with respect to size changes but also to the elemental composition.

Summary and Outlook

SMPS and ICPMS were successfully coupled. A rotating disk diluter was implemented as sample introduction interface which allows aerosol sampling from an undefined environment. This setup allows on-line determination of size distribution and elemental particle composition.

The established measuring setup allows generating nanoparticle containing model aerosols which are used for the validation of SMPS-ICPMS data by comparison to non-modified SMPS instrumentation.

Either volume weighted size distributions have to be calculated from the initially number based SMPS data, or particle number related values have to be computed from the originally mass based ICPMS intensities in order to obtain comparable curves from both sensors. However, good signal correlation was shown after these signal conversions.

The coupled instrumentation was able to clearly distinguish between smaller gold and larger silver particles, and it was shown that dynamic aerosol observation concerning elemental particle composition is possible.

The upcoming work includes the application of the coupled SMPS-ICPMS instrumentation in two research projects, i.e. assessment of nanoparticle containing consumer products and particulate emissions of waste incineration.

Two approaches for reducing the argon consumption of the coupled setup will be investigated. The first is to implement a gas exchange device which allows operating the DMA with air and subsequently replacing the air by argon before the sample aerosol is introduced to ICPMS. The second includes partial or total recirculation of the used sheath gas at the DMA inlet.

Besides, the data processing has to be improved. Correction for multiple elemental charges on particles is going to be implemented, and size and element specific detection limits will be determined from measurements on model aerosols.

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On-Line SMPS-ICPMS Coupling for Simultaneous Analysis of Nanoparticles Concerning Size Distribution and Elemental Composition

24.06.2014

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Introduction

- Characterisation of Airborne Nanoparticles
  - Physical Characterisation (particle size distribution)
    → **Scanning Mobility Particle Sizer (SMPS)**
  - Chemical Characterisation (elemental composition)
    → **Inductively Coupled Plasma Mass Spectrometry (ICPMS)**

- Current Practice:
  - On-line SMPS measurement; time resolution: few minutes
  - EITHER: Off-line size resolved chemical analysis

    Particle Sampling → Sample Handling → Sample Preparation → Off-Line Analysis

  - OR: On-line chemical analysis → no size information

Introduction

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SMPS-ICPMS Coupling:

- On-line physical and chemical particle characterisation
  → Time resolved chemical particle analysis
- No time consuming and error-prone sample preparation
- In-line aerosol sampling, independent of primary aerosol flow
- Application examples:
  - ENP containing sprays
  - Metals in exhaust particles
  - Nano waste incineration

Flow Concept of SMPS-ICPMS Coupling

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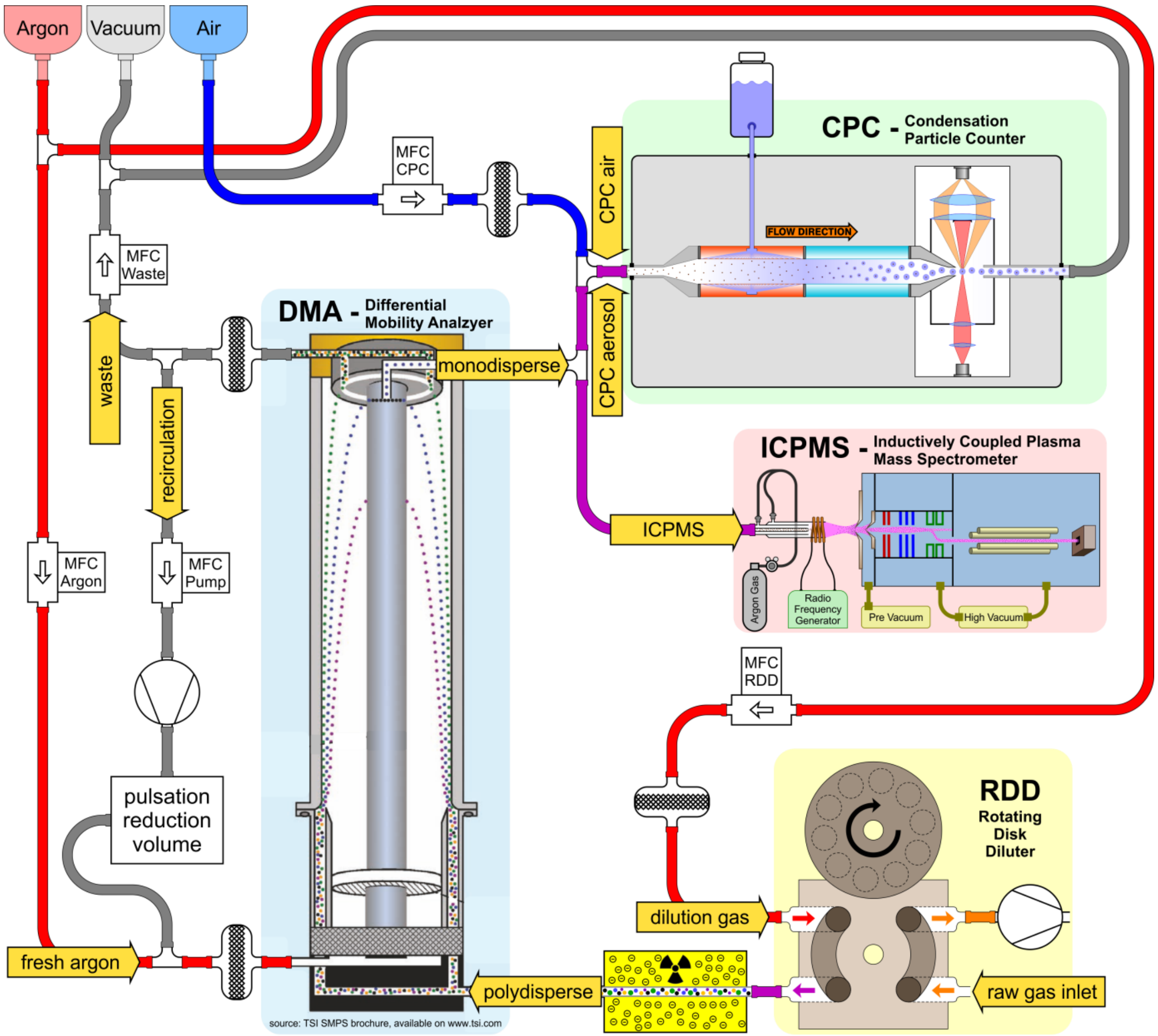


DMA

Differential Mobility Analyser

CPC

Condensation Particle Counter

- Particle **number** signal
- Defined inlet aersosol flow

ICPMS

Inductively Coupled Plasma Mass Spectrometer

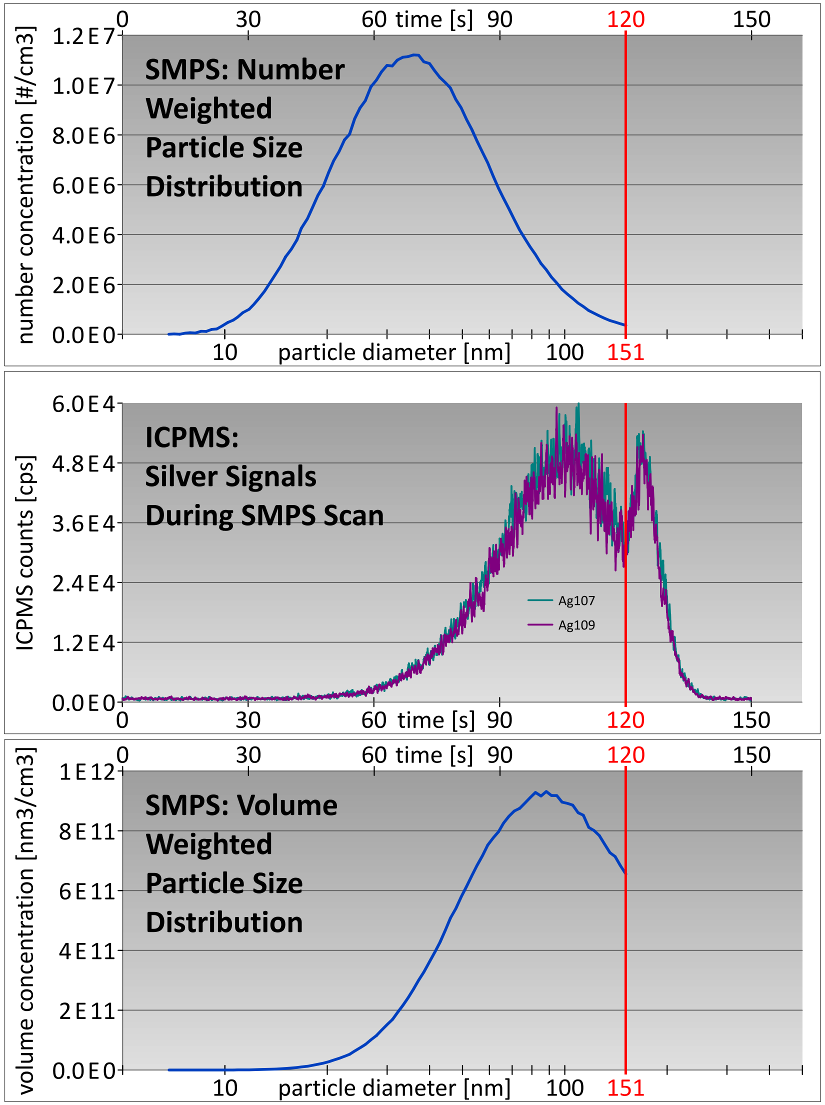
- Argon plasma
- Low air tolerance
- **Mass** related signal
- Inlet flow undefined

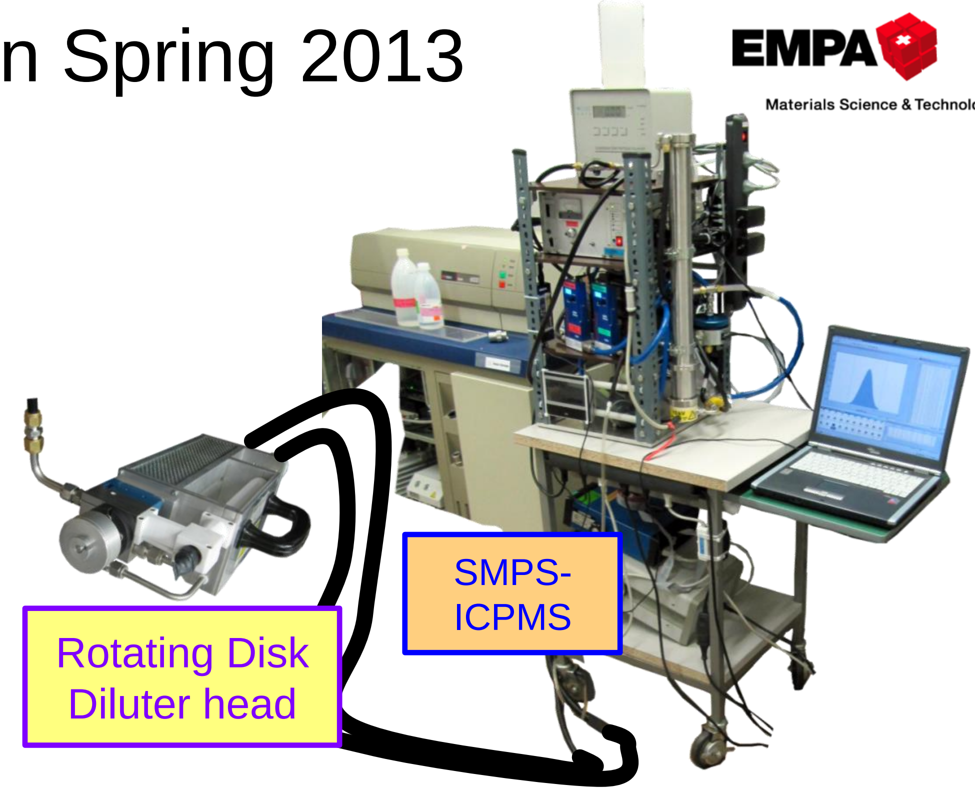
RDD

Rotating Disk Diluter

- Dilution with argon
- Defined DMA inlet flow

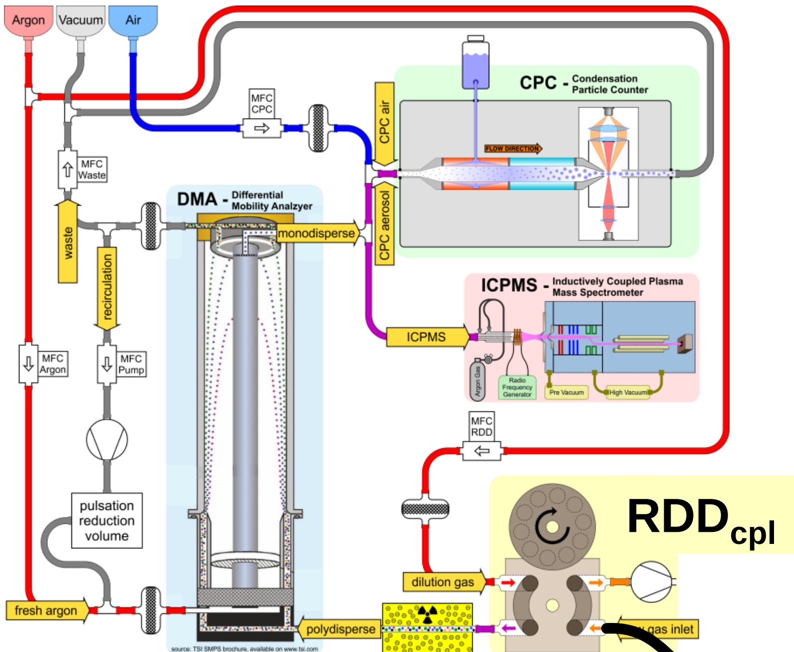
First Coupling Attempt in Spring 2013



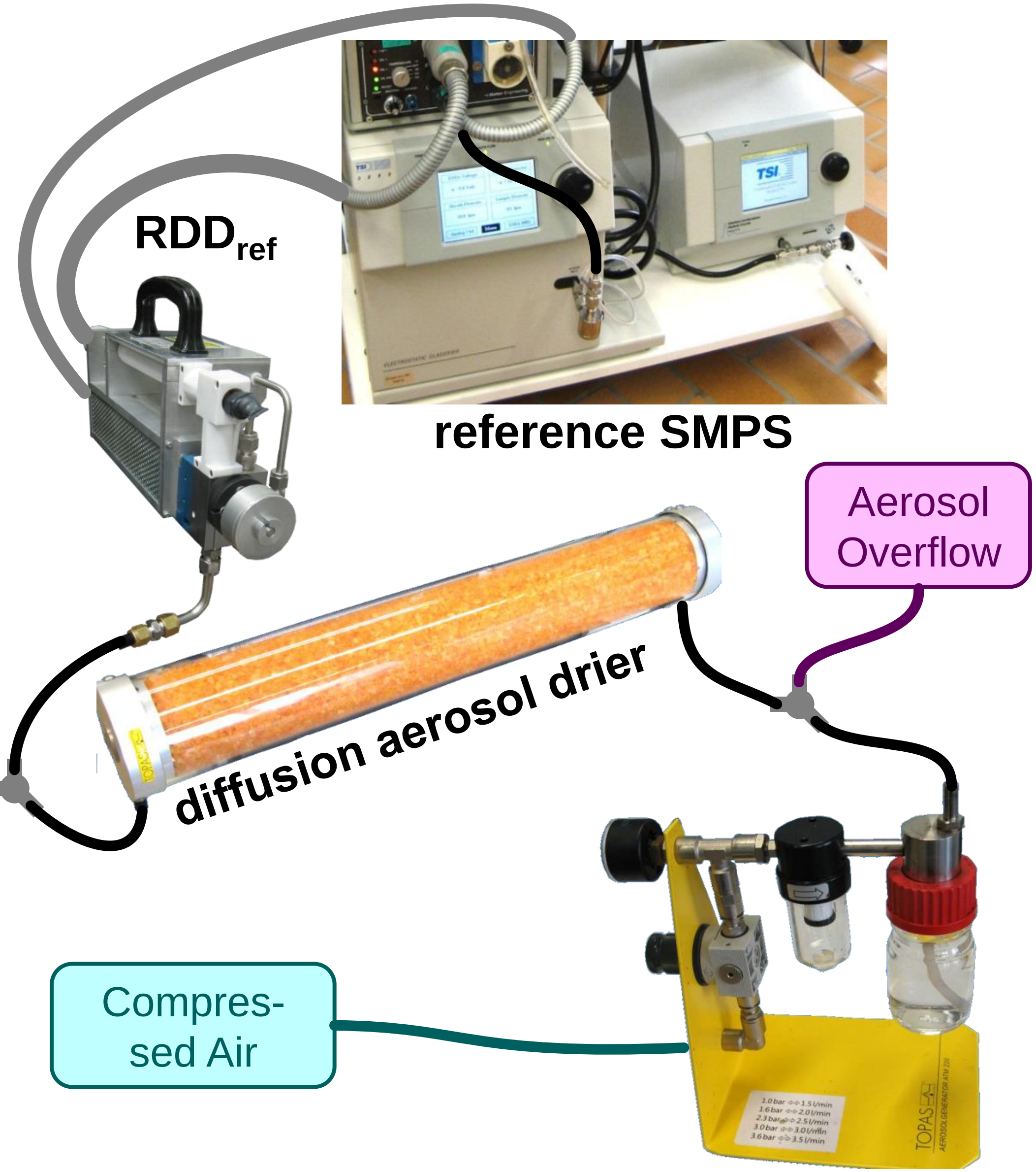


- First successful coupling attempt
- Silver aerosol
- CPC vs. ICPMS signal:
  - CPC: Particle number
  - ICPMS: Element mass
- Single charge probability not yet considered

Measuring Setup



coupled SMPS-ICPMS

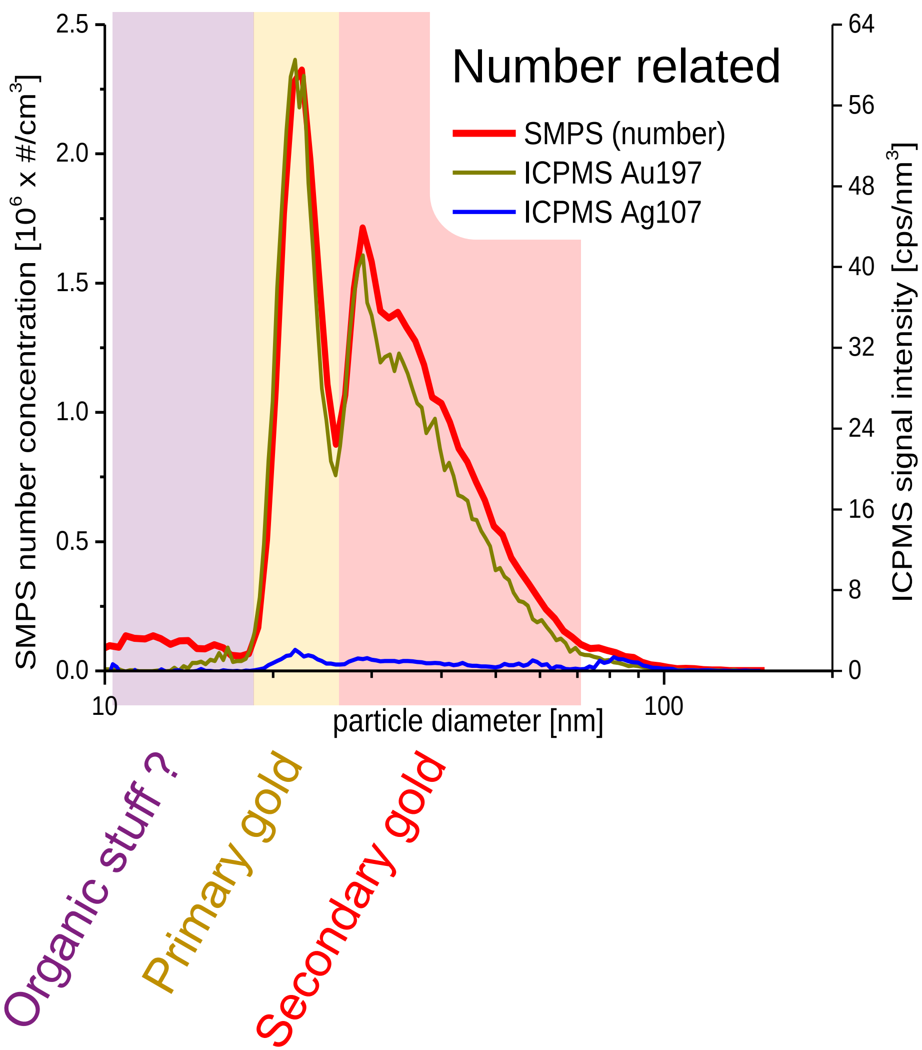


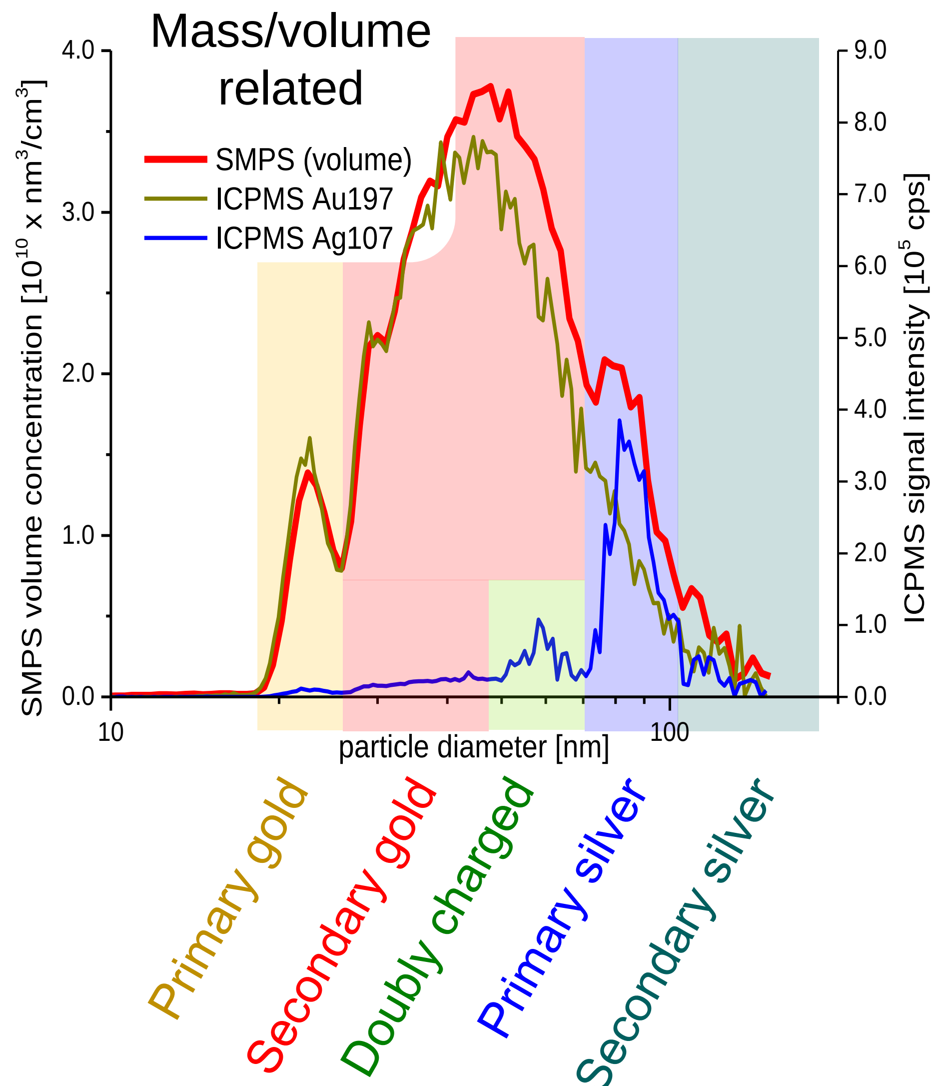
aerosol generator

ICPMS tuning:
- Steady-state aerosol conditions
- Constant DMA voltage

→ Stable signal for calibration

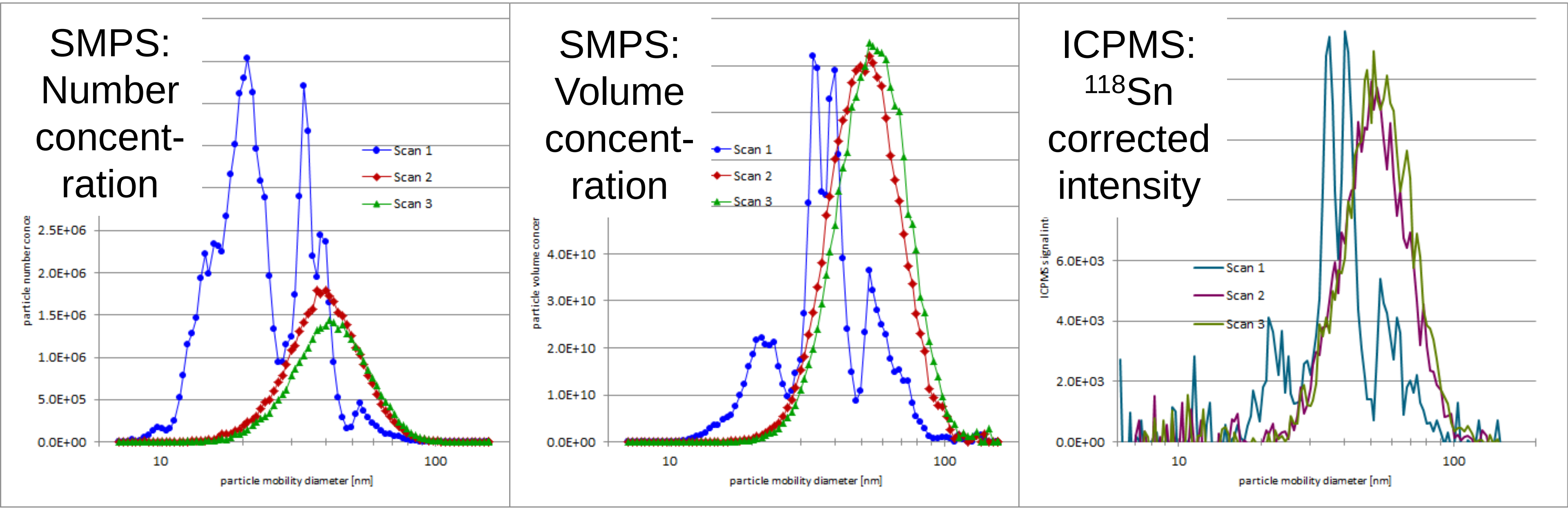
Mixed Gold/Silver Model Aerosol
Number and Mass/Volume Weighted





Real Sample Analysis: NanoSpray Project
Tin particles in dirt-repellent spray

- Number and volume weighed size distribution
- Spray attempt and sampling probe inside glove box
- SMPS-ICPMS scans repeated every 3 min
- Primary 20 nm particles disappear rapidly
- Excellent signal correlation → tin particles identified



Summary

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- Successful SMPS-ICPMS Coupling
- Rotating Disk Diluter to control DMA inlet sample flow
- Simultaneous on-line determination of size distribution and element information
- Measuring setup includes reference SMPS for data validation
- CPC vs. ICPMS signals:
  - Number vs. Mass concentration
  - One has to be computed to be comparable to the other
  - Good correlation between SMPS and ICPMS signals
- Clear discrimiation between smaller gold and larger silver particles
- Dynamic particle observation succeeded

Outlook

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- Application in research projects
  - NanoSpray: Consumer spray products containing ENP
  - NanoWaste: Particulate emissions of incinerated nano-treated materials
- Reduction of argon consumption
  - Gas Exchange Device (air operated DMA)
  - Sheath argon recirculation
- Data processing improvement
  - Size and element specific detection limits
  - Multiple charge correction for ICPMS data

Acknowledgements

- Financial support
  - CCMX
  - R'Equip
- Project collaborators
  - PSI
  - FHNW
  - TSI GmbH
  - HeiQ Materials
  - Matter Aerosol AG
  - NanoSys
- Thesis director and co-director
  - Prof. Dr. Christian Ludwig
  - Dr. Mohamed Tarik

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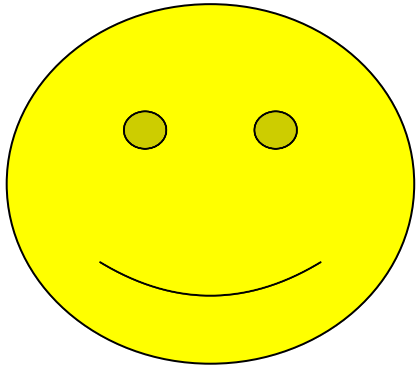

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