Simultaneous Analysis of Size Distribution and Elemental Composition of Airborne Nanoparticles Using an Online-Coupling of SMPS and ICPMS

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Introduction

A detailed characterisation of airborne particles in the nanometre to sub-micrometre size range is mandatory in various fields e.g. risk assessment of products containing engineered nanoparticles or monitoring of combustion generated nanoparticles in emission as well as air quality control.

Knowledge about particle size distribution and size resolved chemical composition obtained with a high time resolution is essential for the monitoring of exhaust aerosols from combustion processes and for a detailed understanding of the dynamic behaviour of nanoparticles. However, most of the available techniques are not able to provide such physical and chemical information simultaneously.

Scanning Mobility Particle Sizer (SMPS) is well established and widely used for physical aerosol characterisation. It provides size distribution and number concentration of particles in a size range from about 5 to 500 nm within scan durations of just some minutes.

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

The coupling of SMPS and ICPMS will allow achieving size and chemical information at the same time. The expected full size range scan duration of several minutes and the even shorter scan times for narrower size ranges will enable transient particle observation, and it opens the possibility to chemically characterise an aerosol in its original condition instead of sampling particles first and analysing them afterwards.

Current Practice

As an example the VERT Secondary Emission Test VSET procedure is illustrated in Fig. 1. This test series is part of the Swiss sustainability test for diesel particulate filter systems [1-4]. These testing setup and procedure are regulated in the Swiss National Standard SN 277 206[5]. Besides a detailed monitoring of particulate matter the VSET test includes also chemical analysis of the fuel fired during the filter tests, determination of the major gaseous pollutants and toxic trace components in the engine exhaust. Fig. 1 gives a brief overview of the VSET procedure and the current practice for size fractionated sampling and elemental analysis of particles.

The particle characterisation includes separate physical and chemical analyses. Aerosol dilution and conditioning is needed for physical particle measurements i.e. determination of size distribution and number concentration. These values are usually obtained by SMPS and a separate sensor providing real-time particle number concentration information.

The SMPS consists of a differential mobility analyser (DMA) and a condensation particle counter (CPC). In the DMA the airborne particles pass between the electrodes of a cylinder capacitor. High voltage between the capacitor electrodes forces the particles to move through an air layer called sheath air between the original carrier gas and the inner capacitor electrode. The high voltage determines which specific particle size exactly reaches the DMA outlet for further analysis, i.e. counting by the condensation particle counter CPC.

The additional chemical characterisation of the particulate fraction makes size-classified sampling with subsequent chemical analyses necessary. Behind a separate dilution tunnel the particles are sampled on a filter for subsequent weighing to determine the total particulate mass concentration, and size fractionated particle collection in a cascade impactor is performed for later chemical analysis using plasma mass spectrometry (ICPMS) which provides elemental composition[6].

The chemical analysis includes an acid digestion of every particle size fraction sample. The resulting liquid samples can then be atomised into an argon atmosphere. The sampled originally particulate matter dissolved in liquid and dispersed in argon passes the argon plasma where it is ionised and is then analysed in the mass spectrometer of the ICPMS.

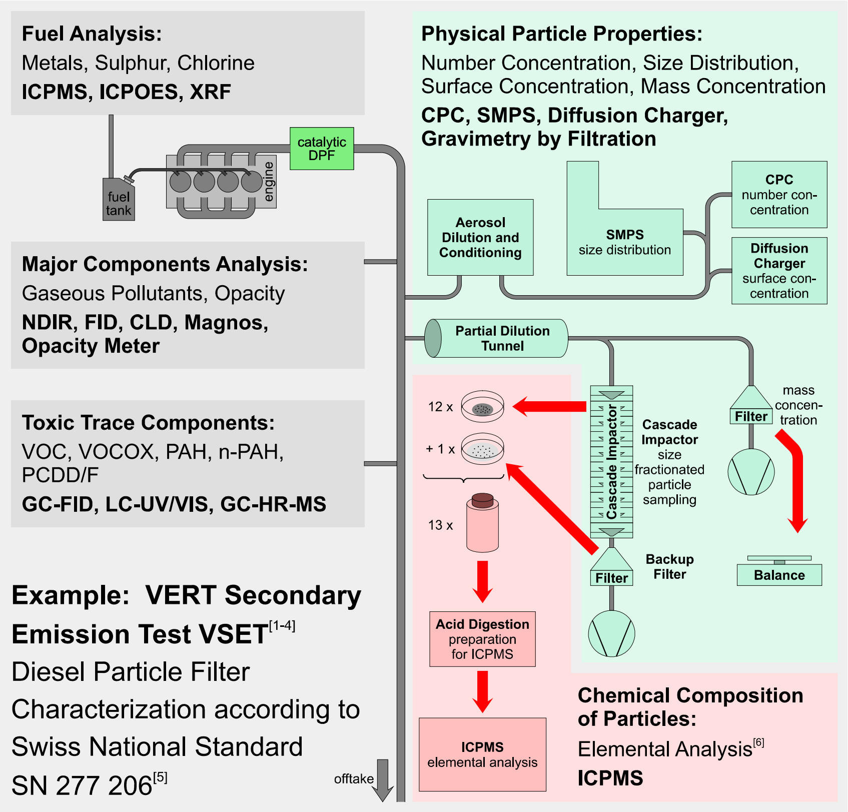

Fig. 1: Current Practice Example: VERT Secondary Emission Test VSET

This analysis procedure allows determining the overall composition of particles which have been collected during a specific sampling duration, i.e. usually during one driving test cycle. It has the following disadvantages:

- Time-consuming procedure due to the separate particle sampling and the different steps of sample preparation for chemical ICPMS analysis.
- Risk of contamination due to transport, storage, and handling of the impactor sampling filters.
- No online information about chemical composition.
- Particle size resolution of chemical analysis limited by number and properties of cascade impactor stages.

Proposed Novel Setup

A coupling of SMPS and ICPMS provides online size and chemical information simultaneously. The DMA selects one particle size class out of the original aerosol. The number concentration is then determined by the CPC as it is done in standard SMPS configuration, while the ICPMS connected in parallel to the CPC determines the elemental composition. This is done for the whole particle size range.

Since the nanoparticles are already dispersed in gas they can be directly introduced to the plasma of the ICPMS without the need of additional sampling, digestion and re-dispersion.

This novel setup provides the following benefits:

- Simultaneous information on particle size and chemical composition.
- Short scan durations of some minutes allowing quasi on-line elemental composition measurements.
- Size distribution and multi element information.
- Direct monitoring of transient processes.
- Elemental analysis of aerosols in their original conditions without separate sampling and sample preparation.

Flow Concept for the SMPS-ICPMS Coupling

The planned setup is outlined in Fig. 2. Since the air tolerance of the argon plasma at the ICPMS inlet is limited to about 10 to 20 %, the DMA needs to be modified ensuring the transfer of the particles from air to argon atmosphere. Thus, the DMA acts as a kind of gas exchanger for the originally airborne particles. Therefore the sheath gas layer has to consist of argon instead of air in standard SMPS operation. To lower the argon consumption, it is intended to partly recycle the argon used as sheath gas.

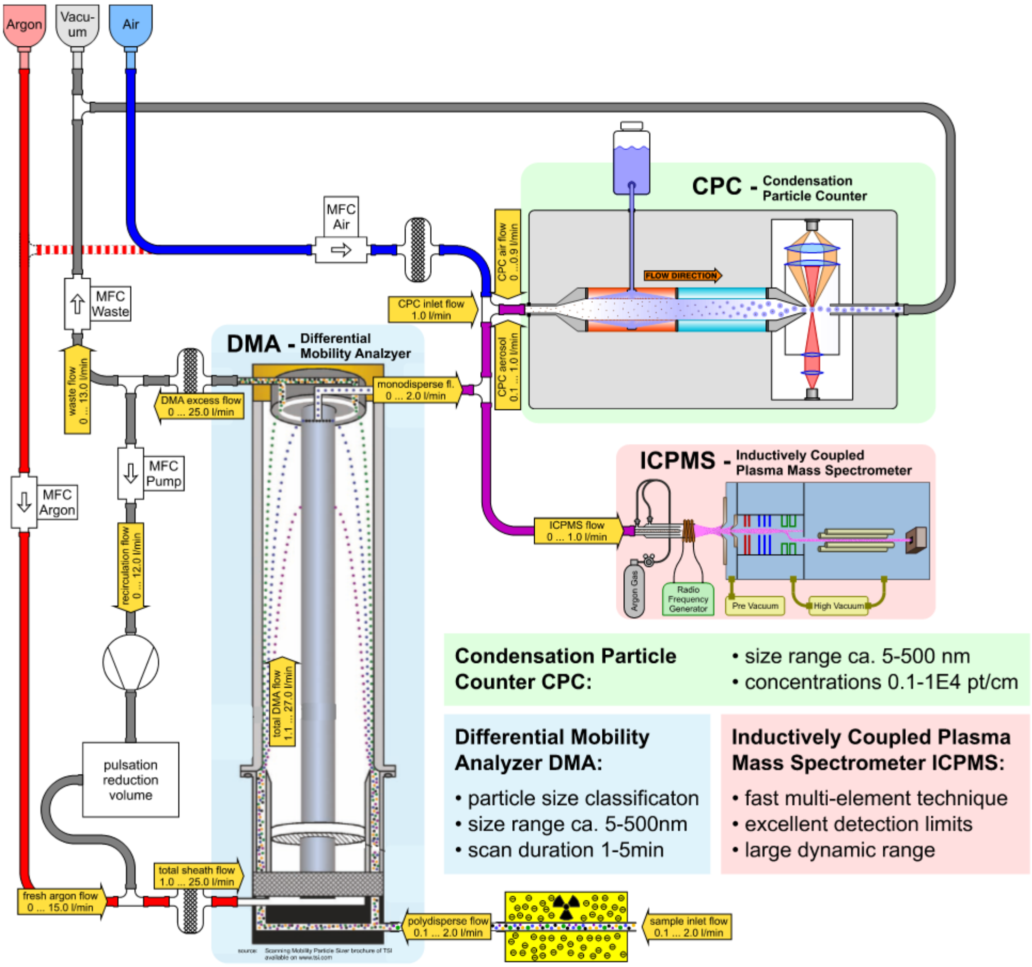

Fig. 2: Flow Concept of the Novel Setup

The DMA polydisperse sample inlet and monodisperse outlet have normally the same volume flow which means also the excess out and the sheath in flow have to be equal. Therewith basically the excess flow can be filtered and fed back to the sheath gas inlet, which usually is done in modern SMPS systems.

With this setup an air enrichment of the excess / sheath gas flow is expected since the polydisperse aerosol at the DMA inlet consists of airborne particles while the particles at the monodisperse aerosol outlet will be mainly dispersed in argon. Therefore at least a partial replacement of the excess gas by fresh argon is needed. For this aim a series of mass flow controllers are added to the SMPS setup allowing variable excess gas recirculation rates from 0 to 100 %.

The argon carried monodisperse particles at the DMA outlet are split into a CPC and an ICPMS fraction. An additional mass flow controller allows adding argon or filtered air to the CPC inlet. This causes some extra particle concentration reduction at the CPC inlet but it enables to adjust the monodisperse flow entering the CPC and therewith to set variable flow fractions to the two sensors located downstream the DMA.

Challenges and Expected Limits

The DMA of the SMPS has to be operated using sheath argon instead of sheath air since the ICPMS requires the measured particles to be carried in argon with a relatively low oxygen tolerance.

A sheath gas flow up to 15 l/min will be needed depending on the desired particle size range limits. Therefore it makes sense to take argon saving measures. The flexible flow concept allows variable DMA inlet and outlet flows including the possibility of up to 100 % excess / sheath gas replacement. It is estimated that about 50% recirculation will lead to over 90 % argon purity which is expected to be sufficient.

The behaviour of particles when transferred into argon atmosphere is expected to be different to that of airborne particles. Hence, a new calibration of DMA and CPC is needed.

Even if the detection limits of ICPMS are extremely low a certain amount of particulate matter molecules are needed. It is possible to detect e.g. single silver particles with 20 nm diameter operating an ICPMS in single element analysis mode. But the particle number concentration at the DMA monodisperse outlet has to be higher if several elements have to be detected or if the particles are even smaller than 20nm.

A high particle concentration, low number of analysed chemical elements and low particle size resolution or narrow measured size range will allow scan durations which might be similarly short as in standard SMPS operation where a scan usually takes about 1 to 5 min.

Scan durations will be enhanced by scanning broad size spectra with high size resolution and by measuring high numbers of detected elements.

Acknowledgements

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Introduction

Monitoring of airborne nanoparticles:
- ➡ number concentration, size distribution
- ➡ chemical composition

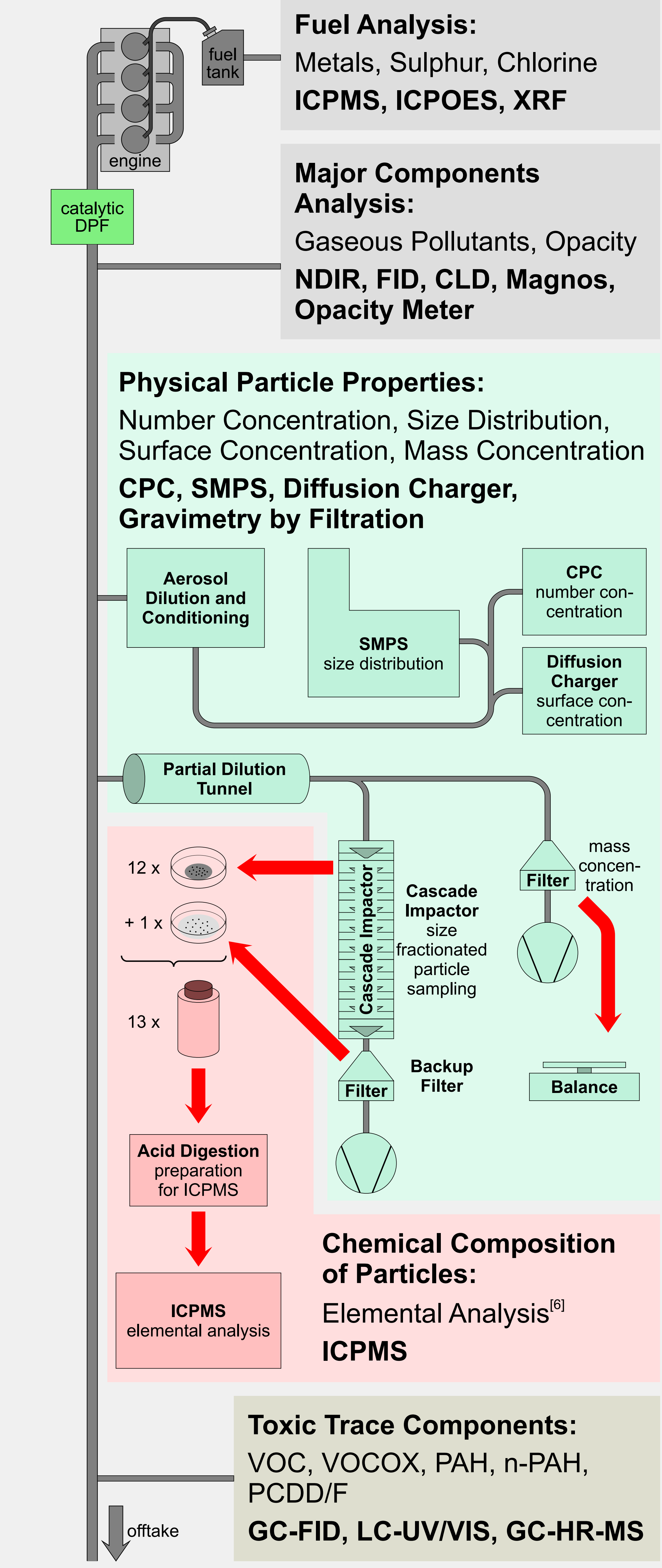
Scanning Mobility Particle Sizer (SMPS):
- ➡ size distribution and number concentration

Inductively Coupled Plasma Spectrometry (ICPMS):
- ➡ elemental composition

Coupling of these two techniques
- ➡ simultaneous size and chemical information

Current Practice

Example: VERT Secondary Emission Test VSET[1-4]
Diesel Particle Filter Characterization according to Swiss National Standard SN 277 206[5]



Fuel Analysis:
Metals, Sulphur, Chlorine
ICPMS, ICPOES, XRF

Major Components Analysis:
Gaseous Pollutants, Opacity
NDIR, FID, CLD, Magnos, Opacity Meter

Physical Particle Properties:
Number Concentration, Size Distribution, Surface Concentration, Mass Concentration
CPC, SMPS, Diffusion Charger, Gravimetry by Filtration

Chemical Composition of Particles:
Elemental Analysis[6]
ICPMS

Toxic Trace Components:
VOC, VOCOX, PAH, n-PAH, PCDD/F
GC-FID, LC-UV/VIS, GC-HR-MS

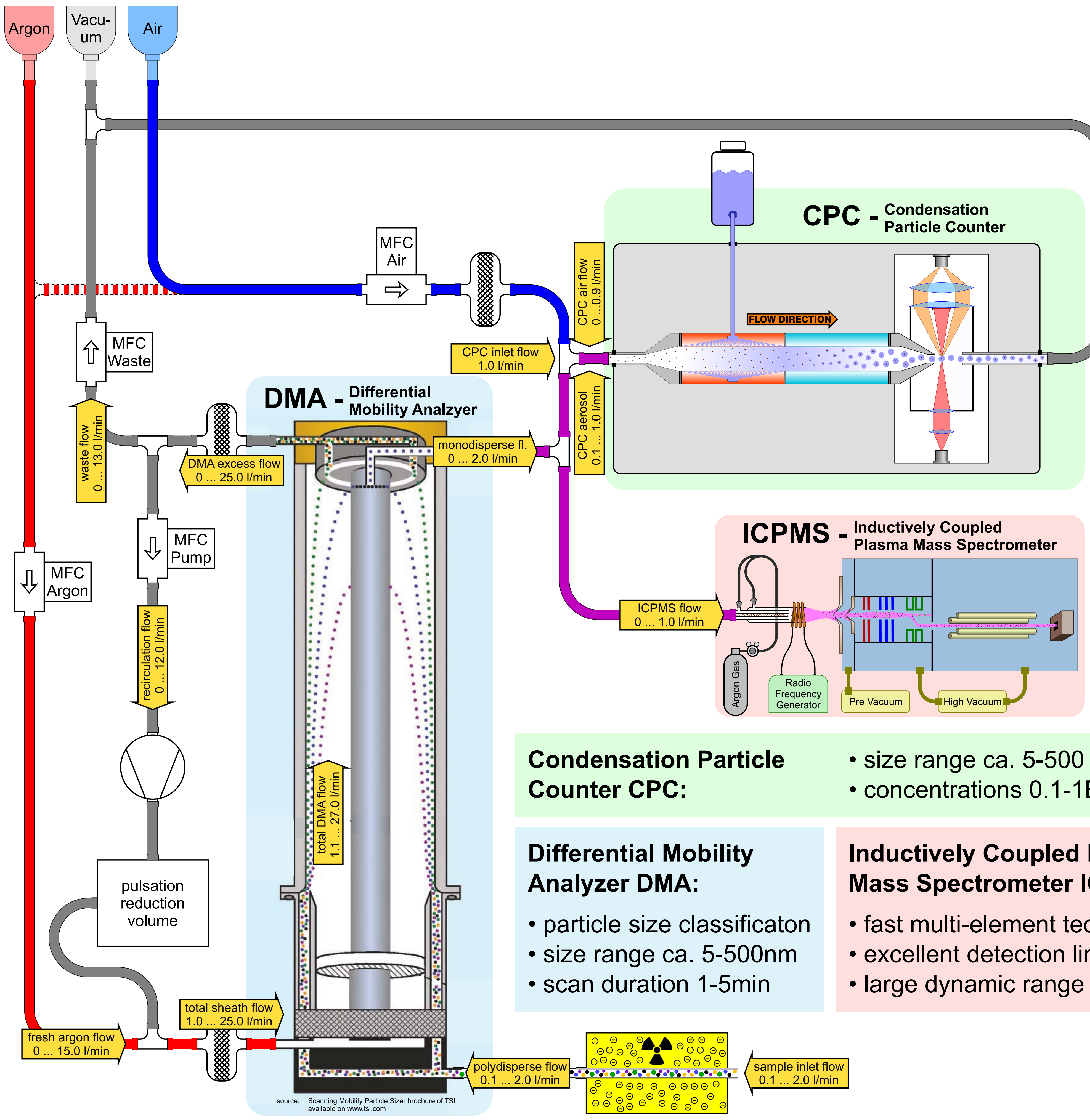
Disadvantages Current Practice

- ☹ **separate sampling and chemical analysis**
- ☹ **time-consuming sample preparation**
- ☹ **risk of contamination**
- ☹ **no online chemical information**

Benefits of the Novel Setup

- ☺ **simultaneous information on particle size and chemical composition**
- ☺ **short scan duration of a few minutes**
  - ➡ **quasi-online technique**
- ☺ **size distribution and multielement information**
- ☺ **direct monitoring of:**
  - **- transient processes and changes**
  - **- aerosols in original conditions**

Flow Concept for SMPS-ICPMS Coupling



source: Scanning Mobility Particle Sizer brochure of TSI available on www.tsi.com

Condensation Particle Counter CPC:
- size range ca. 5-500 nm
- concentrations 0.1-1E4 pt/cm

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

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

Challenges and Expected Limits

ICPMS Operated with Argon Plasma
air tolerance of ICP: ca. 10...20%vol
➡ **DMA has to be operated with sheath argon instead of air**

Large ArgonConsumption (Sheath Gas)
argon saving measures requested
➡ **Flexible flow concept**
- sheath and/or sample gas reductions
- 90% purity expected @ 50% argon recirculation

ICPMS Limits Of Detection
minimum amount of particle molecules needed for ICPMS detection
➡ **Single particle detection possible**
e.g. Ag particles: 20nm in single element analysis
multi element / smaller particles: higher concentration

SMPS Scan Duration Limits
sequential mass spectrometer limits scanning rate
➡ **modern quadrupol ICPMS: down to 1ms per mass**
- analysis duration depends on number of elements
- wider SMPS channel width enhances particle concentration and reduces scan duration

Acknowledgements

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Literature

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