Particle characterisation

Methods applied for the characterisation of fine particulate emissions

Thomas Brunner

Austrian Bio Energy Centre

Institute for Process Engineering
Graz University of Technology
TEL.: +43 (316) 481300; FAX: +43 (316) 4813004
E-MAIL: thomas.brunner@tugraz.at
HOMEPAGE: http://RNS.TUGRAZ.AT

Contents

- Introduction
  - Relevance of particle characterisation
  - Relevant characteristics of fine particulate emissions from biomass combustion
- Particle characterisation technologies applied
- Conclusions and outlook

Introduction (I)

- **Relevance of the characterisation of fine particulate emissions from small-scale biomass combustion.**

  - Gain more **detailed information about particle formation** during small-scale biomass combustion and the mechanisms involved.

  - Provide information to **interlink the properties of PM emissions** from small-scale biomass combustion plants **with characteristics of ambient air PM**.

  - **Future aim:**
    provide information about characteristics of PM emissions from biomass combustion for a **classification of their toxicity**.

Introduction (II)

➢ **Relevant characteristics of fine particulate emissions from biomass combustion**

- **Particle size distribution**
  - mass-size distribution
  - number-size distribution
- **Shape and structure of the particles**
- **Chemical composition**
  - inorganic compounds
  - organic compounds and soot
  - PAHs

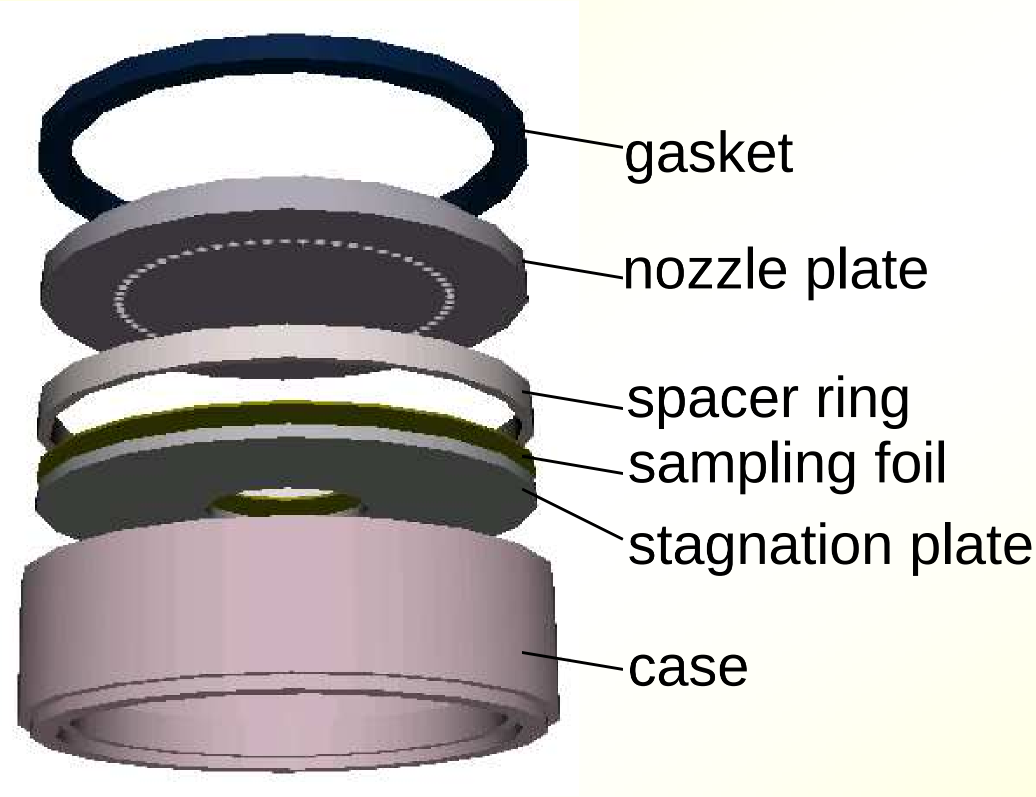
Particle size distribution – general issues

- **Results from various research projects show that**
  - in small-scale biomass combustion plants almost no coarse fly ash particles are emitted,
  - more than 90% of the total PM emissions are related to PM_{10},
  - there is an almost neglectable amount of particles in the size range between 1 and 10 µm and therefore, PM_1 almost equals PM_{10}.
- **Consequently, to determine the particle size distribution of PM emissions from small-scale biomass combustion plants, mainly the size range <1 µm is of interest.**

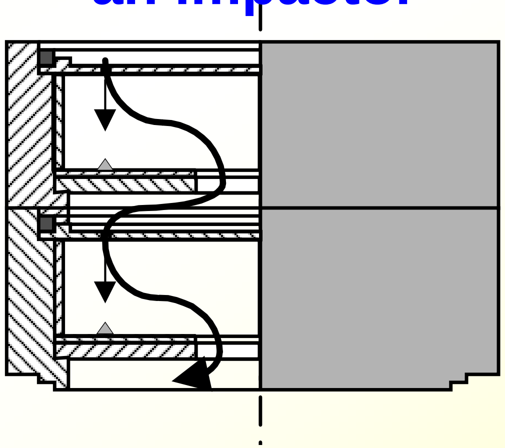
Institute for
Process Engineering
Graz University of Technology

Discontinuous determination of the particle size distribution – impactors (I)

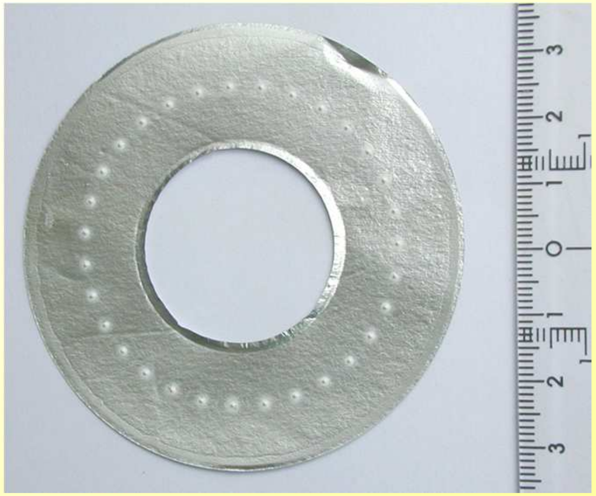
scheme of a single separation stage of a Berner-type low pressure impactor



particle separation in an impactor



sampling foil with particles



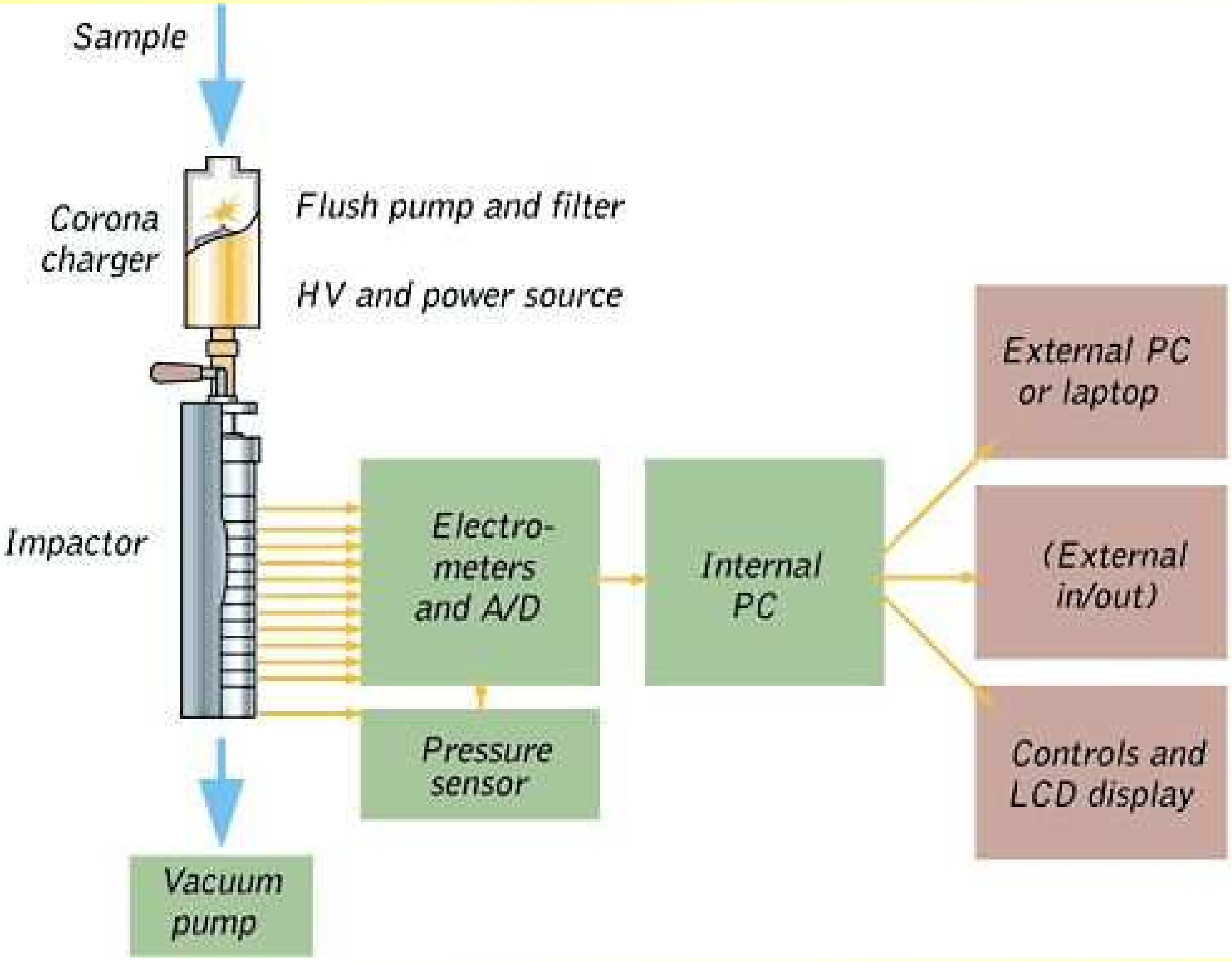
Discontinuous determination of the particle size distribution – impactors (II)

device	remarks	advantages	disadvantages
PM_{10} impactors	- usual cut diameters: 10 µm, 2.5 µm, 1 µm, final filter stage - aerodynamic diameters	- gravimetric method - easy to apply - subsequent chemical analyses of particles sampled possible - no dilution needed	- low resolution regarding particle sizes - no information about PSD <1 µm - discontinuous measurement
Low pressure impactors	- cut sizes from some 10 nm to some µm - aerodynamic diameter	- gravimetric method - various substrates can be applied - subsequent chemical analyses possible - no dilution needed	- discontinuous measurement - time consuming - short sampling time if no dilution is applied

Explanations: diameters in µm aerodynamic diameter, PSD … particle size distribution

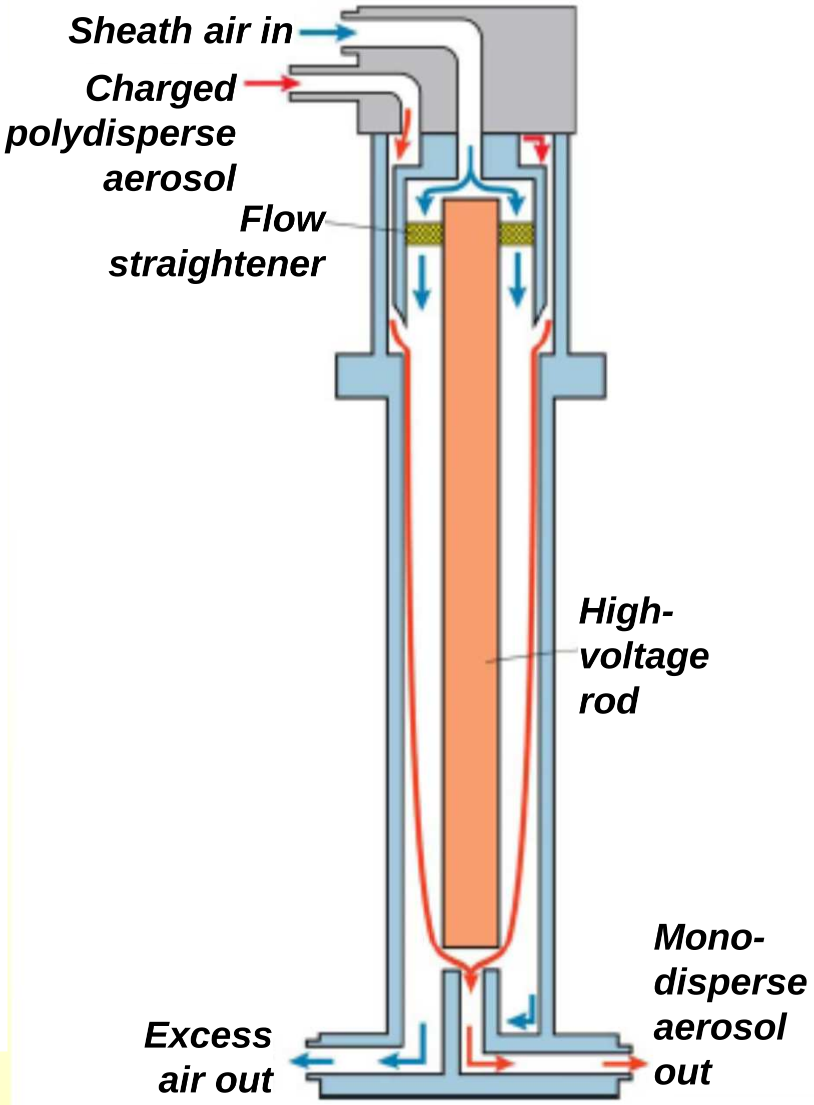
On-line determination of the particle size distribution (I)

Electrical Low Pressure Impactor



source: http://dekati.com/cms/elpi

Scanning Mobility Particle Sizer



source: http://www.tsi.com

On-line determination of the particle size distribution (II)

device	remarks	advantages	disadvantages
ELPI (electrical low-pressure impactor)	- 0.03 - 10 µm - aerodynamic diameter	- robust - indicates changes in process well - large size range	- overestimation of agglomerates and coarse particles - dilution needed
SMPS (scanning mobility particle sizer)	- 0.005 - 1 µm - 0.003 - 0.09 µm - electrical mobility diameter	- very small particles can be detected - high resolution	- long scanning time (problem in varying combustion process) - dilution needed
FMPS (fast mobility particle sizer)	- 0.005 - 0.560 µm - electrical mobility diameter	- fast - indicates changes in process well	- more inaccurate than SMPS - high dilution ratios needed

Particle size distribution – aerodynamic and electric mobility diameter

Aerodynamic diameter (ae.d.):

- Generally, PM are not of uniform shape and density.
- The aerodynamic diameter is used to make particles comparable.
- It is the diameter of a spherical particle with a density of 1 g/cm³ that has the same inertial properties in air as the particle of interest.

Electric mobility diameter

- SMPS and FMPS systems are based on DMAs (differential mobility analysers), where charged particles are separated by an electrostatic classifier.
- Therefore, they are classified according to their electric mobility diameter.

Particle size distribution – general remark concerning measurement results

- **From low-pressure impactors information about the mass-size distribution of particles based on aerodynamic diameters is gained.**

- **The ELPI provides information about the number-size distribution of particulate matter based on aerodynamic diameters.**
  The determination of the mass-size distribution from the number size distribution is problematic since several particle properties have to be known (shape, density, etc.).

- **SMPS and FMPS results are given as number-size distributions and are based on electric mobility diameters.**

- **These differences have to be considered when comparing measurement results gained from these devices.**

Chemical characterisation

Parameters of interest

- **Major ash and aerosol forming elements:**
  e.g.: K, Na, S, Cl, Ca, Si, Mg, Mn
- **Heavy metals:**
  e.g.: Zn, Cu, Cd, Pb
- **Carbonaceous compounds**
  OC … organic carbon
  EC … elemental carbon (soot)
  IC … inorganic carbon (carbonates)
- **PAH**
  16 PAHs according to EPA

Chemical characterisation – major and minor ash forming elements

➢ Wet chemical analyses

- ☺ different sampling substrates applicable (metal foils, quartz filters)
- ☺ low detection limits can be achieved
- ☹ only bulk-analyses possible

➢ Electron microscopy

- ☺ different sampling substrates applicable
- ☺ structural analyses of single particles are possible if appropriate sampling methods are applied
  (single particles and no bulk samples are needed)
- ☹ compared to wet chemical analyses less sensitive

Chemical characterisation – wet chemical analyses (I)

Digestion

- Cl: eluation (24h) with bi-distilled water
- all others: multi-step pressurised digestion with $HNO_3/HF/H_3PO_4$

Detection

- Cl: ion chromatography (IC)
- all others: adsorption spectrometry (AAS) or plasma emission spectrometry (ICP-MS, ICP-OES)

Chemical characterisation – wet chemical analyses (II)

Restrictions concerning wet chemical analyses of impactor samples

- **Sample mass needed: >50 µg**
- **With increasing sample mass the accuracy of the analyses increases. However, usually only 2 to 3 impactor stages with sufficient particle mass can be provided.**
- **Therefore, a micro balance with high resolution must be used in order to avoid weighing errors which later can cause incorrect analyses results.**
- **To increase the sample mass and therefore also the accuracy, a mixed sample of more than one impactor stage can be made.
However, thereby information about the differences of the chemical compositions of different particle size classes is lost.**
- **Especially during field tests assembling and disassembling of the sampling device usually take place under conditions different to a clean room. It has to be taken care that the samples are not contaminated during sample handling, storage and transport.**

Chemical characterisation – electron microscopy

Technologies applied

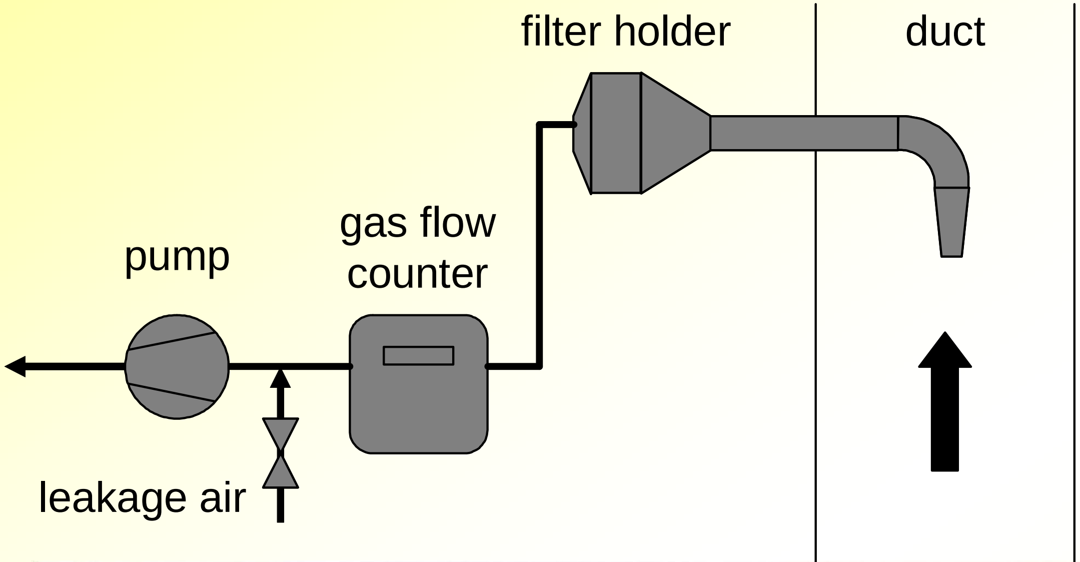
- Scanning electron microscopy (SEM)
- Transmission electron microscopy (TEM)
- Energy dispersive x-ray spectrometry (EDX)

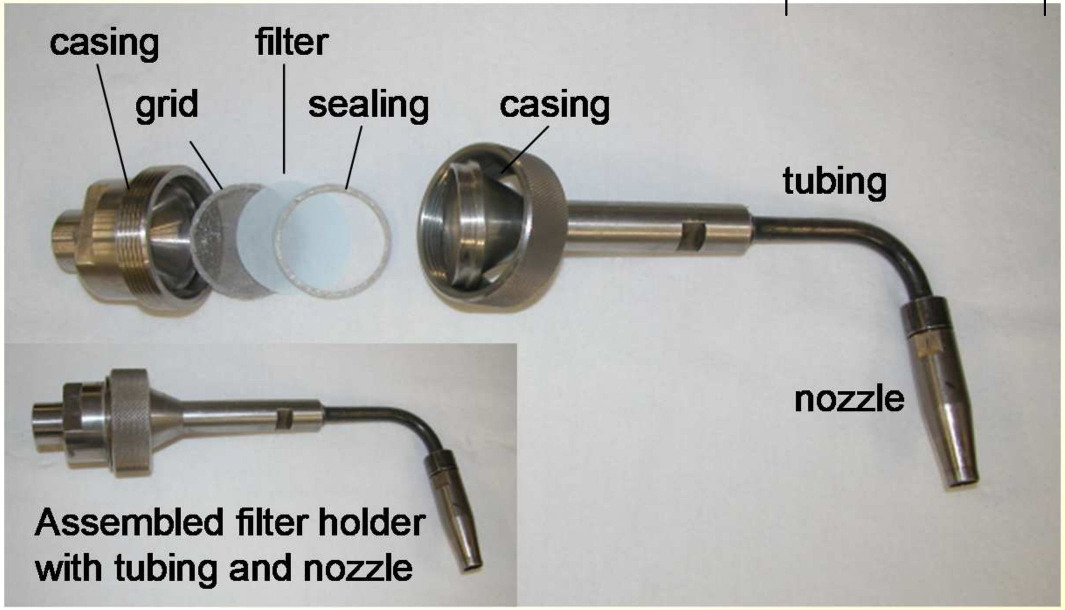
Restrictions for SEM

- If the surface of the sample is not perfectly plane, the electron beam is scattered and signals from the sample surface next to the particle are detected together with signals from the particle.
- The penetration depth of the electron beam can be greater than the particle size ➔ also signals from the substrate are detected.
- The sample usually has to be coated to make it electroconductive. The element chosen for coating (in many times C but also Au and others are applied) can thus not be detected correctly.
- Detection limit: usually ~1 wt%
  calibration with standard materials is recommended

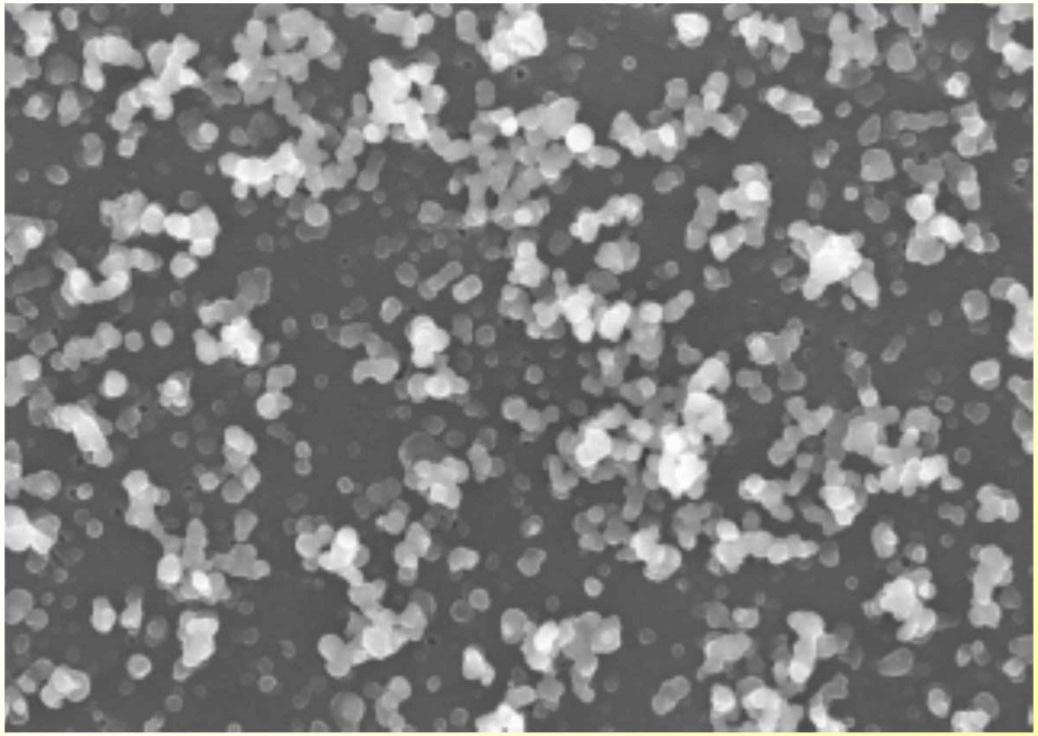
Chemical characterisation – particle sampling for electron microscopy (examples)

Sampling with a polycarbonate filter





Assembled filter holder with tubing and nozzle

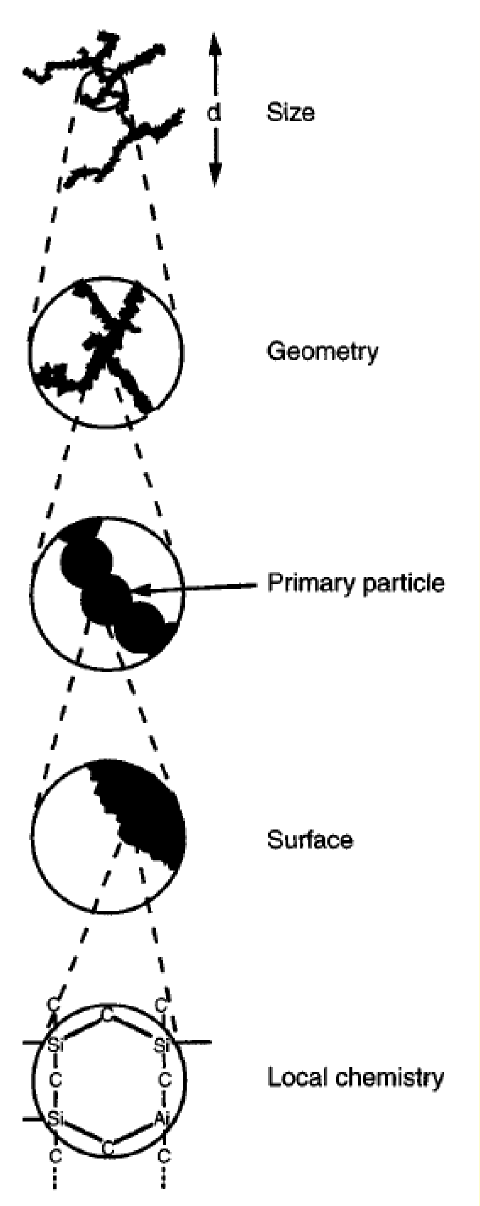


samples taken downstream the boiler
during a combustion test with bark
picture widths: 5.6 µm

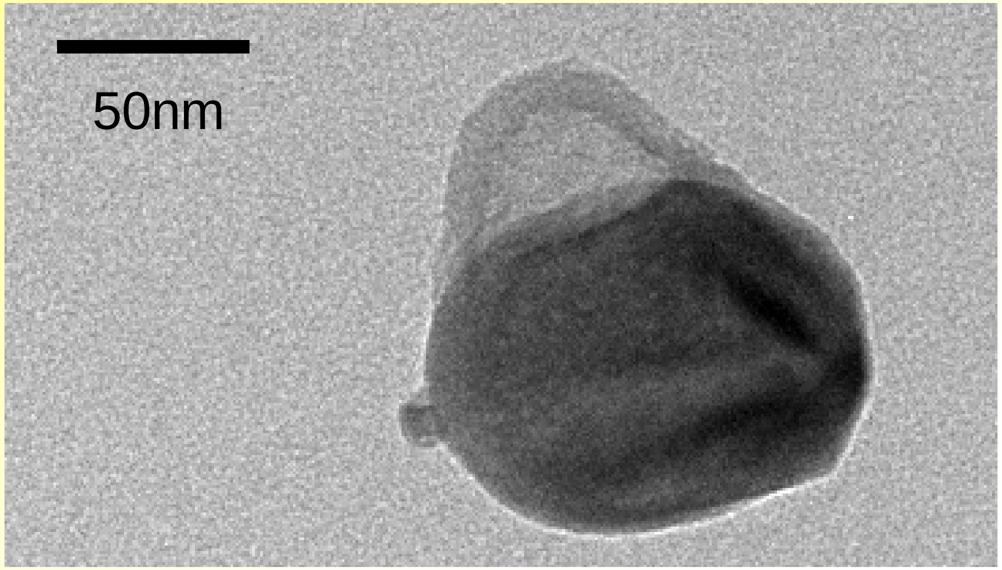
Chemical characterisation – particle sampling for electron microscopy (examples)

Individual agglomerates can be collected on EM grids and then be analysed

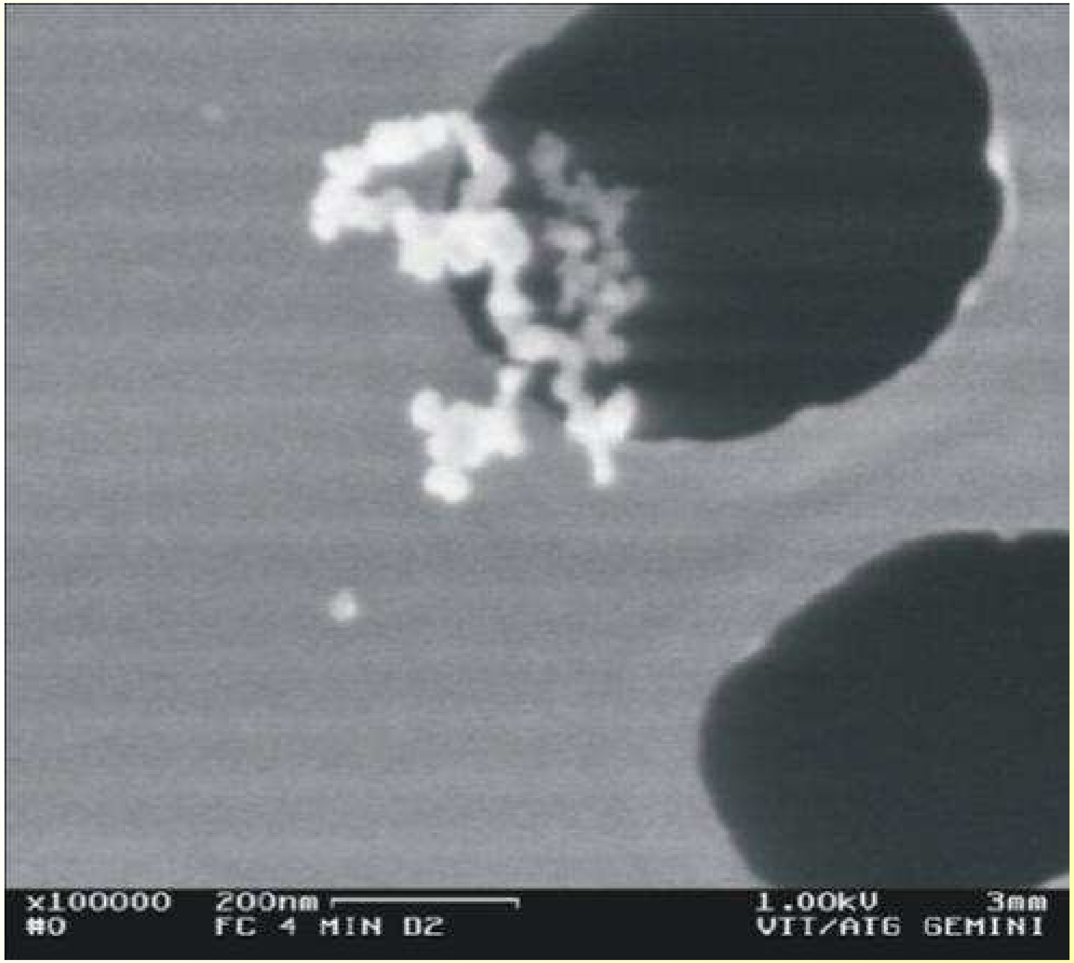
Source: University of Kuopio
Fine Particle and Aerosol Technology Laboratory
Dept. of Environmental Science



Chemical characterisation – electron microscopy - examples



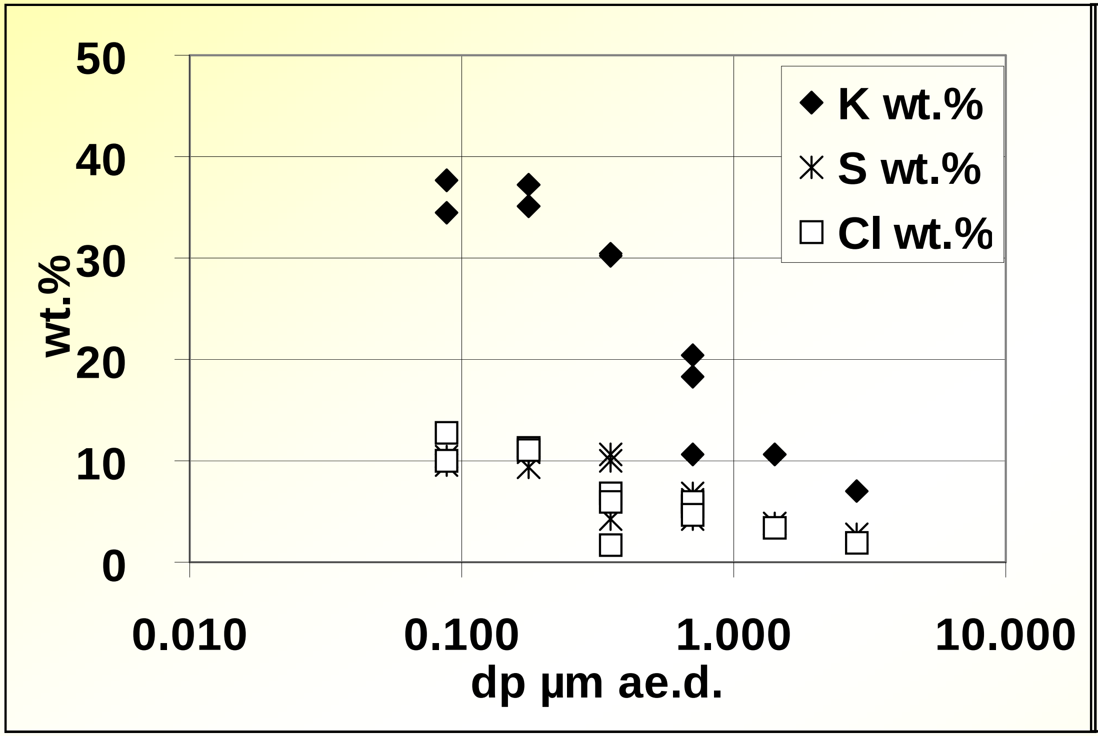
- TEM/EDX micrograph of an aerosol particle sampled during beech combustion (good burnout conditions)
- sampling with a Cu-grid
- dark zone:
  mainly K and S with traces of Cl
- bright zone:
  mainly K and Cl with traces of S



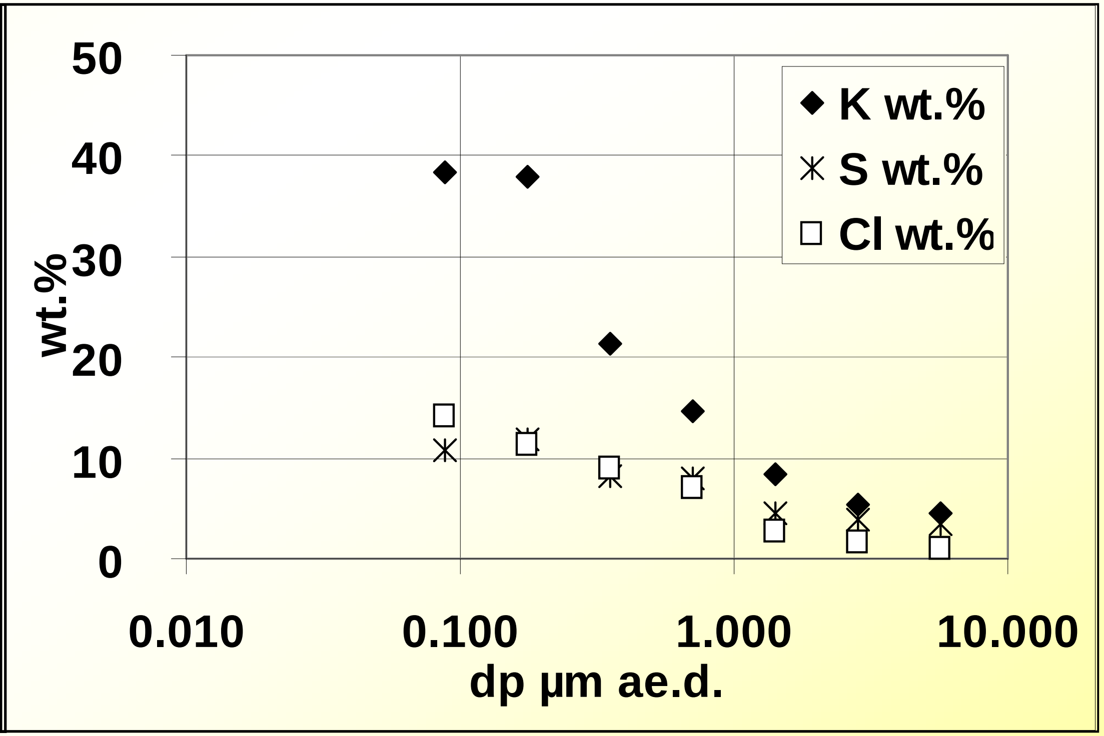
- SEM image of a soot agglomerate sampled during poor burnout conditions
  (source: University of Kuopio
  Fine Particle and Aerosol Technology Laboratory,
  Dept. of Environmental Science

Chemical characterisation – comparison of results from wet chemical and SEM/EDX analyses

SEM/EDX analyses



wet chemical analyses



Explanation: sample from wood chip combustion;
sampling with a low-pressure impactor on Al sampling foils; the sampling foils were cut into two pieces of which one was forwarded to SEM/EDX and the other one to wet chemical analyses;
ae.d. … aerodynamic diameter

Chemical characterisation – carbonaceous compounds (I)

- **General remark**
  When sampling particles on a filter, besides the particles also absorbed gaseous compounds are collected. This has to be considered for substrate treatment, sampling and analyses.

- **Compounds of interest**
  - **OC … organic carbon**
  - **EC … elemental carbon**
  - **IC … inorganic carbon (carbonate)**

- **Detection of inorganic carbon and sum of OC and EC with a C-analyser**
  - **The sample is heated under oxidising conditions up to 1,000°C.**
  - **A Cu-catalyst transforms C-species to CO_2 which is detected by ND-IR.**
  - **CO_2 detected below 550°C is allocated to reactions of elemental and organic carbon ➔ non carbonate carbon (OC + EC).**
  - **Signals detected at temperatures >550°C are allocated to carbonates.**

Chemical characterisation – carbonaceous compounds (II)

➢ Detection of OC and EC (thermo-optical methods)

- The sample is heated according to a defined temperature program.
- Carbonaceous species are released from the sample and are converted in catalysts to CO_2.
- The CO_2 is either
    - detected by a ND-IR analyser or
    - reduced to CH_4 which is detected with a FID.
- The filter transmittance is permanently monitored with a laser to correct for charring effects.
- Due to the fact that a laser is used to correct for charring effects, the sampling media applied must allow transmission (no analyses of metal impactor foils possible).

Chemical characterisation – carbonaceous compounds (III)

➢ Method according to NIOSH 5040

- **OC is determined under He-atmosphere at 300°C, 470°C, 610°C and 865°C**
- **EC is determined under an atmosphere containing 2% O_2 and 98% He at 550°C, 620°C, 700°C, 780°C, 850°C and 865°C**
- **Detection by using a FID**

➢ Method according to Puxbaum et al.

- **Sample is heated continuously (20°C/min) to 800°C in O_2 atmosphere.**
- **CO_2 detection by a NDIR analyser.**
- **The first peak in CO_2 that evolves after the transmission has reached again the initial value is assigned to EC**
  (the corresponding temperature is around 350-450°C).
- **All previous peaks are assigned to OC.**
- **IC causes another distinct peak which evolves after the EC peak at about 600°C.**

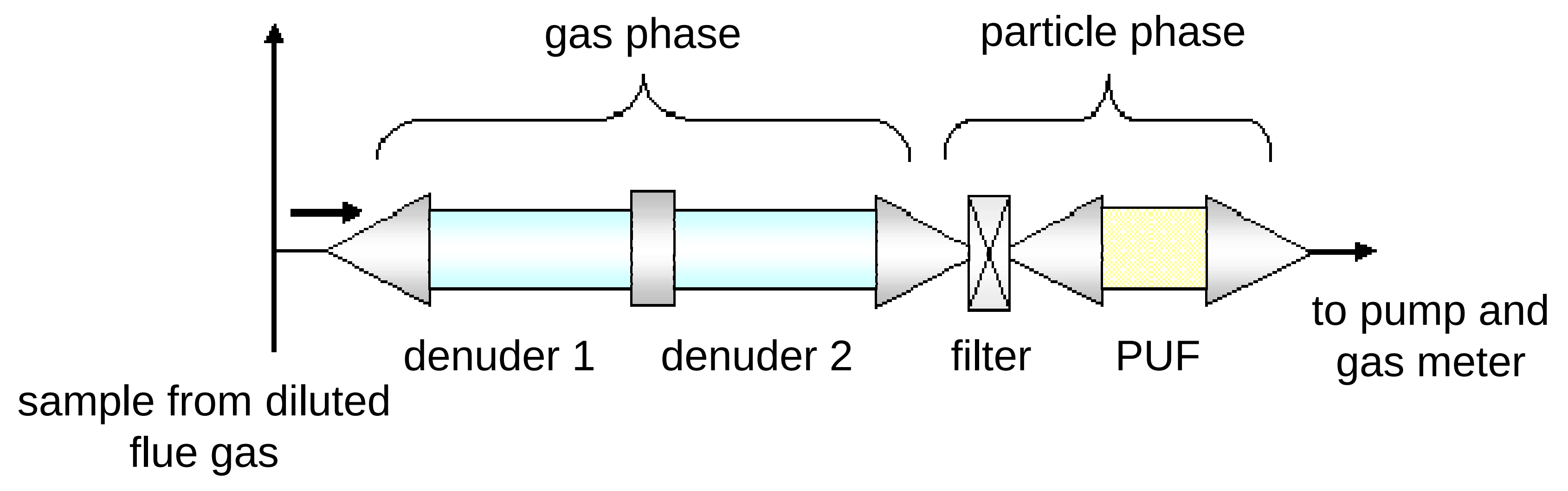
Chemical characterisation – PAH concentrations (I)

➢ General approach

- **Sampling of gaseous and particulate phase PAHs on adsorbents/filters.**
- **Detection of PAHs by GC/MS from the extracts of adsorbents and filters.**

➢ Denuder Method

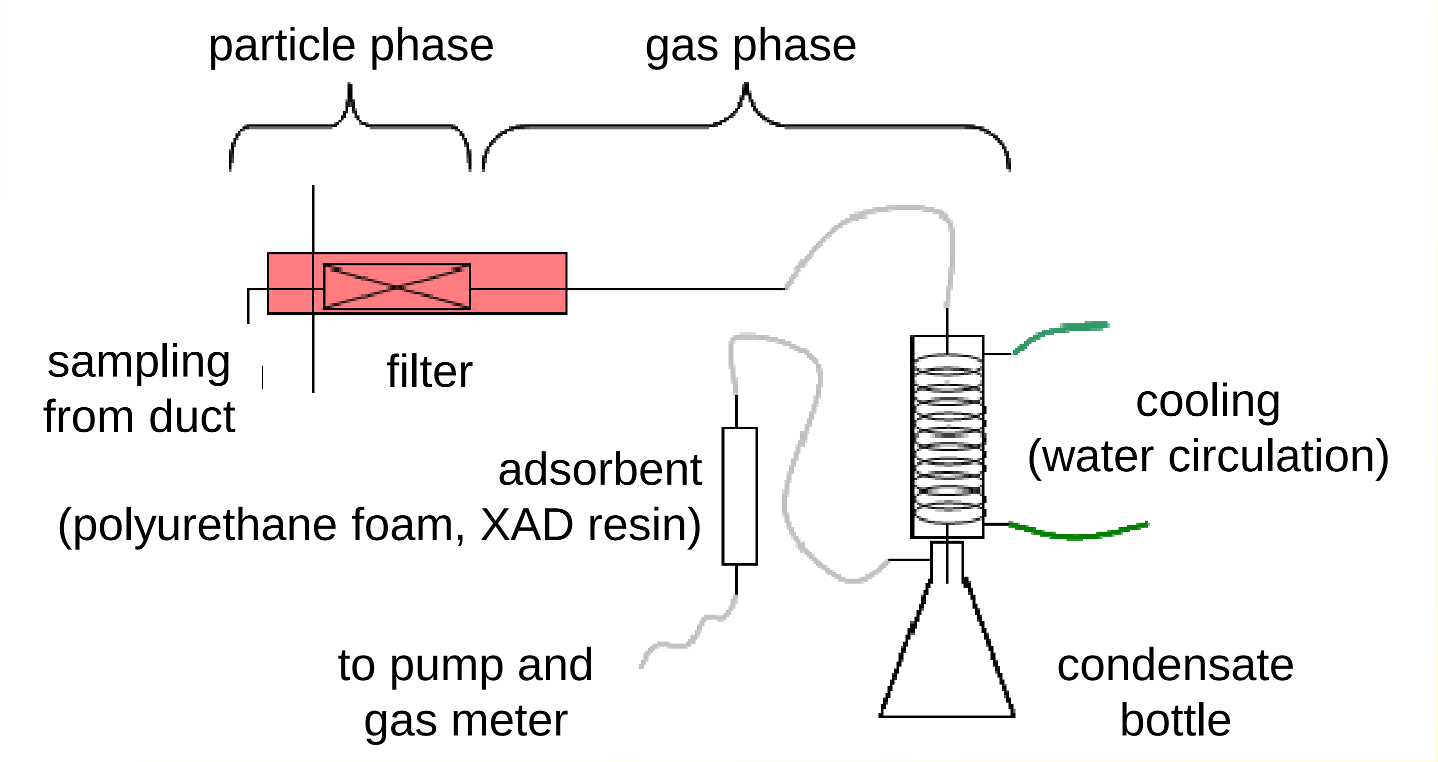
- **Applied when sampling from diluted exhaust gas.**
- **Denuders, filter and polyurethane foam (PUF) are extracted separately.**



Chemical characterisation – PAH concentrations (II)

➢ Filter-cooler method

- **Applied when sampling from undiluted (hot) exhaust gas.**
- **Particle phase and gas phase are sampled separately.**
- **It has to be considered, that during the cooling of the flue gas between the stove/boiler and the chimney outlet PAHs condense and therefore the distribution between gas and particle phase is changed.**



Conclusions and outlook (I)

- **For the characterisation of fine particulate emissions from biomass combustion a broad range of different technologies is applicable.**

- **Particle size distribution**
  - **The information gained from the different instruments applied significantly differs in:**
    - **resolution concerning particle sizes**
    - **time resolution**
    - **mass or number-size distribution**
    - **aerodynamic and electric mobility diameter**

  These differences have to be considered regarding the selection of a certain measurement method as well as concerning the evaluation of the results.

Conclusions and outlook (II)

- For structural and chemical characterisation of particulate emissions proven methods are available.
  The following issues have to be considered:
  - The sampling substrate and its pre-treatment has to be tailored to the demands of the analyses method applied.
  - Special care has to be taken during substrate preparation, sampling, sample storage and sample transport in order to avoid contaminations.
- Presently, technologies for on-line analyses of PM are gaining rising interest (e.g.: aerosol mass spectrometers).
  However, these devices are, compared with off-line methods expensive and only limited experiences (especially concerning emission measurements) are available so far.

Acknowledgement

BIOMASS - PM Project

ERA-NET Bioenergy project Biomass-PM
Clean biomass combustion in residential heating
particulate measurements, sampling, and physicochemical and toxicological characterisation

FFG

NACHHALTIGwirtschaften

Energiesysteme der Zukunft

eine Initiative des Bundesministeriums für Verkehr, Innovation und Technologie (BMVIT)

bmvit

Thank you for your attention

Dipl.-Ing. Dr. Thomas Brunner
Inffeldgasse 21b, A-8010 Graz, Austria
TEL.: +43 (316) 481300; FAX: +43 (316) 4813004
Email: thomas.brunner@tugraz.at
HOMEPAGE: http://www.rns.tugraz.at