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The SMPS, the Most Widely Used Nanoparticle Sizer

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Introduction to the Presentation "The SMPS, the Most Widely Used Nanoparticle Sizer" at the 2. ETH-Workshop on „Nanoparticle Measurement", Zürich, 7. August 1998

The Scanning Mobility Particle Sizer (SMPS) has been used for many different research applications involving particles in the nanometer size range. Today it is the most widely used on-line instrument to measure particles in that size range. The SMPS has proved especially useful for applications where the size and number of ultrafine particles are of interest. For combustion aerosols, the majority of the particle number can be found in the nanometer size range while it represents in many cases less than 1% of the particle mass. Auto companies and engine-research institutes use the SMPS successfully to characterize nanoparticles in exhaust emissions. The principal motivation for measuring these vehicle and, particularly, diesel emissions is that they have been linked to causing human health problems.

The scope of this presentation is to give insight into the operation of the SMPS as well as to look at the accuracy and uncertainty of SMPS measurements. The SMPS is the only instrument that gives fast, reliable and repeatable results in the nanometer size range but for the Electrical Low Pressure Impactor (ELPI). However, although an excellent choice for studies of engine driving cycles and PM 10 related measurements, the ELPI only has seven size classes below 1 micrometer. In the same sub-micrometer range the SMPS offers an unmatched resolution of 147 size classes. For this reason researchers have found the SMPS to be an excellent choice for high-resolution measurements under steady state conditions while the ELPI is the preferred instruments to measure rapidly changing size distributions. Due to the wide concentration range the SMPS is suitable to measure both directly at the tailpipe or from dilution tunnels. It can be used for diesel and gas engine emission measurements, as well as for applications involving the characterization of catalysts or alternative fuels (for example, low-sulfur diesel), or the design of particle traps.

After a description of the SMPS operating principle its main components - the differential mobility analyzer (DMA), the aerosol neutralizer, and the Condensation Particle Counter (CPC) - are explained in detail. A thorough study at the National Institute of Standard & Technology (NIST) in Gaithersburg, MD, is used to show the overall accuracy of the SMPS. In the NIST study a repeatability of 14 SMPS measurements of c_v= 0.2% and a total random uncertainty of 0.00055 µm for measuring atomized 0.1 µm polystyrene latex particles (PSL) were determined. Next, SMPS limitations for dynamic measurements are explained. Due to the minimum 30 to 60 seconds required for a full scan, no second-by-second analysis for the whole size range can be achieved. However, it is possible to build up a "picture" of the size distribution by running multiple tests over a cycle at different sizes. Also, some advice to users is given and attention is paid to things like classifier flow settings, counting statistics and SMPS scan times to minimize systematic and statistical errors. Finally, some aspects of the general measurement conditions like the importance of well-designed sampling systems, transport lines and dilution tunnels are mentioned.

Overview

- Short system description
- SMPS components & accuracy
  - Electrostatic Classifier
  - Aerosol charging
  - Particle detector: CPC
  - Estimation of total uncertainty
- SMPS advantages
- Limitations
- Things to pay attention to

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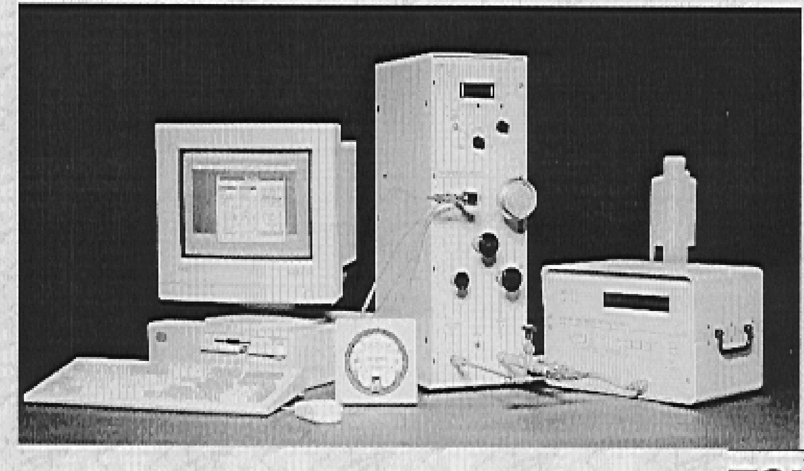
Scanning Mobility Particle Sizer (SMPS)



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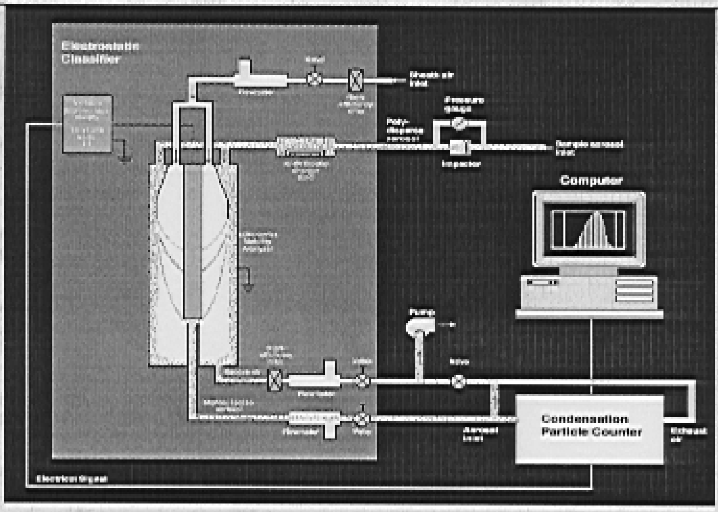
SMPS Principle

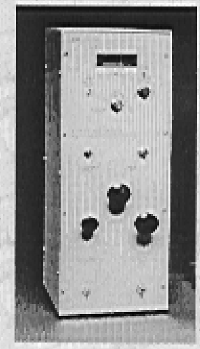
- Pre-impactor
  - removes coarse particles
- Neutralizer
  - well-defined bipolar charge equilibrium
- DMA classification
  - acc. to electrical mobility
  - defined size (+) steered into slit of rod (-)
  - exit: monodisperse aerosol
- CPC: concentration / size class

Flow Schematic of SMPS



Electrostatic Classifier

- Generates monodisperse submicron aerosols
- Performance depends on:
  - flow, electric field & p. transport
- Limitations:
  - below 10 nm (Fissan et al.):
    - deposition losses & Brownian diffusion
    - broad DMA transfer function
  - aerosol charging



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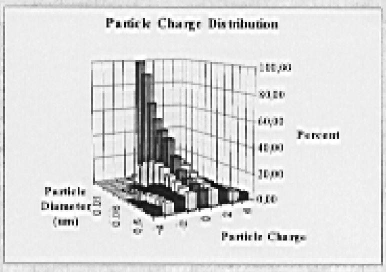
Aerosol Charging

- Radioactive neutralizer Kr-85
  - Beta emissions create bi-polar ions
- Charging not ideal
- Fuch's charge dist.
  - few nano p. charged
  - multiple charging of large particles
  - 0.1 µm: 24% +1 charge, 4% +2
- SMPS charge correction



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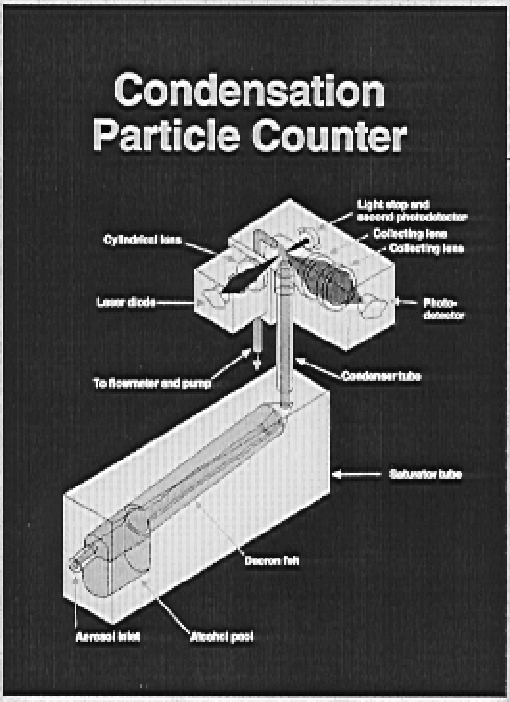

CPC Operation

- particles enter, saturated with butanol vapor
- cooled to induce super-saturated condition
  - condensation on particle
  - growth, near uniform size
  - droplets large enough for:
- simple opt. detector
  - A) ind. particles counted
  - B) add. int. of scat. light

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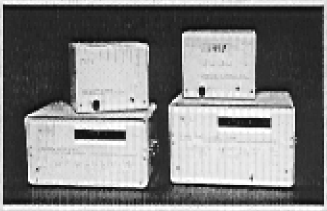
Using the Correct CPC

- High concentration aerosols
  - Model 3022A (10^7 P/cc)
  - (or Model 3025A)
- Low concentration
  - Model 3010 (1 L/min)
- Fastest response time
  - Model 3025A (1 s)
  - (or Model 3010)



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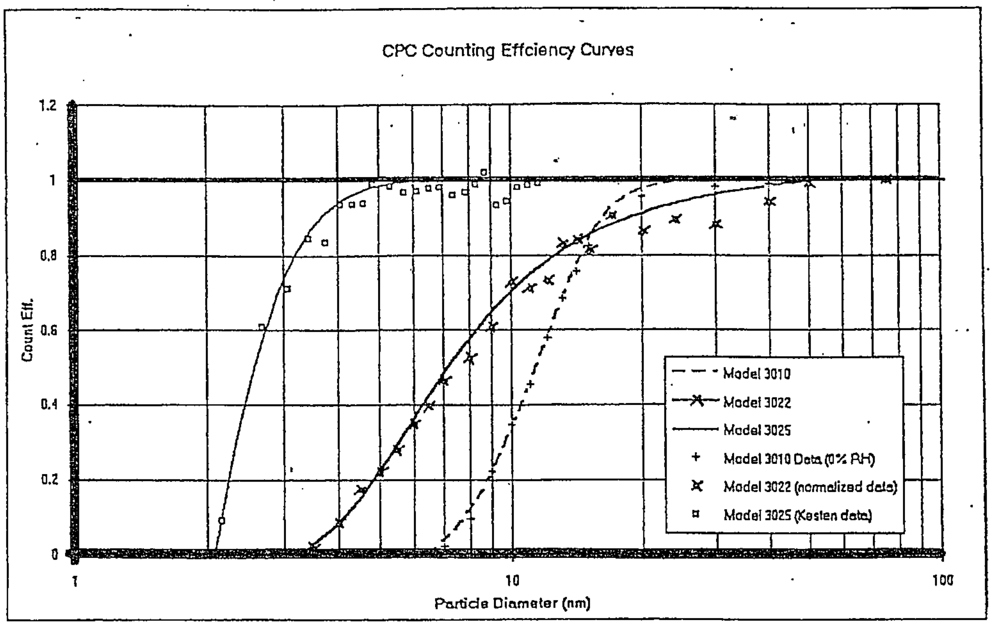
Particle Detector

- Condensation Particle Counter
  - nearly ‘universal’ detector
  - wide size & conc. range
  - no calibration (VDI 3489)
- Limitation:
  - too low or too high conc.
    - dilution when above specs
- CPC accuracy:
  - extreme conc. accuracy (single particle counting)
  - counting effic.: ~100% from 0.02 - 1 µm



SMPS Advantages

- Reliable nanometer sizes
  - for stable aerosols ("steady state")
- Features:
  - ✓ 0.005 to 1 µm
  - ✓ wide concentration range
  - ✓ high resolution: 147 classes (<u>submicron</u>)
  - ✓ number based
  - ✓ excellent repeatability

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Overall SMPS Accuracy

- Detailed study at NIST
  - determined accuracy of "EC method"
  - develop accurate 0.1 µm size standard
    - "all phys. variables in size equation accurately known"
- Results (for 0.1 µm PSL) :
  - repeatability of 14 meas.: cv= 0.2%
  - random error: 0.1%
- Total uncertainty: +3% / -3.3%

  (incl. H_2O impurity)

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Use of the Electrostatic Classification Method to Size 0.1 μm SRM Particles—A Feasibility Study

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The use of the electrostatic classification method for sizing monodisperse 0.1 μm polystyrene latex (PSL) spheres has been investigated experimentally. The objective was to determine the feasibility of using electrostatic classification as a standard method of particle sizing in the development of a 0.1 μm particle diameter Standard Reference Material (SRM). The mean particle diameter was calculated from a measurement of the mean electrical mobility of the PSL spheres as an aerosol using an electrostatic classifier. The performance of the classifier was investigated by measuring its transfer function, conducting a sensitivity analysis to verify the governing theoretical relationships, measuring the repeatability of particle sizing, and sizing NIST SRM 1691, 0.269 μm and NIST SRM 1690, 0.895 μm particles. Investigations of the aerosol generator's performance focused on the effect of impurities in the particle-suspending liquid on the resulting particle diameter.

The uncertainty in particle diameter determined by electrical mobility measurements is found to be −3.3% to +3.0%. The major sources of uncertainty include the flow measurement, the slip correction, and a dependence of particle size on the aerosol flow rate. It was found that the classifier could be calibrated to indicate the correct size to within 0.1% for both SRM particle sizes if the defined classification length is decreased by 1.9%.

Key words: aerosol generator; atomizers; condensation nuclei counters; electrical mobility; particle size; polystyrene latex spheres.

Accepted: November 20, 1990

National Institute of Standards & Technology

Certificate

Standard Reference Material 1963

Nominal 0.1 μm Diameter Polystyrene Spheres

This Standard Reference Material (SRM) is intended primarily for use as a primary reference standard for the calibration of particle size measuring instruments including optical and electron microscopes. The SRM consists of 5 mL of carboxylated polystyrene spheres in water at a weight concentration of about 0.5%. It is supplied in a dispensing vial.

The number average particle diameter was measured in air as an aerosol by electrical mobility measurements. The certified value is:

Number Average Diameter, μm	Uncertainty, μm
0.1007	± 0.0020

The uncertainty includes both random and systematic errors. The total random uncertainty is 0.00055 μm (95% confidence interval), and a conservative estimate of the systematic error is 0.0014 μm.

The size distribution of the polystyrene spheres, as determined by electrical mobility measurements, is narrow with a standard deviation of 0.0018 μm excluding outliers. The number of undersized particles is negligible and the number of oversized particles (diameters greater than 0.2 μm) is less than 0.1%.

SMPS Limitations

- Dynamic measurements
  - * full scan minimum 30 to 60 s
  - * no s-to-s analysis
  - * single size over cycle
    - multiple tests of discrete sizes build “picture”
    - sum of particles ≠ total N
- Rapidly changing dist.
- Below 10 nm less accurate
- Extreme concentrations
  - * (→ next slide)

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Things to Pay Attention to

- Classifier flows influence size
  - * set precisely & verify (i.e. Gilibrator)
- Particle concentration:
  - * too high cause coincidence problems; dilute
  - * too low: poor statistics; increase scans / sample
- Size range:
  - * wider ranges have poorer “statistics” / class
    - “zoom” into range of interest
- Scan time:
  - * fast scans might “smear” data
    - reduce from 300 s until distribution “shifts”

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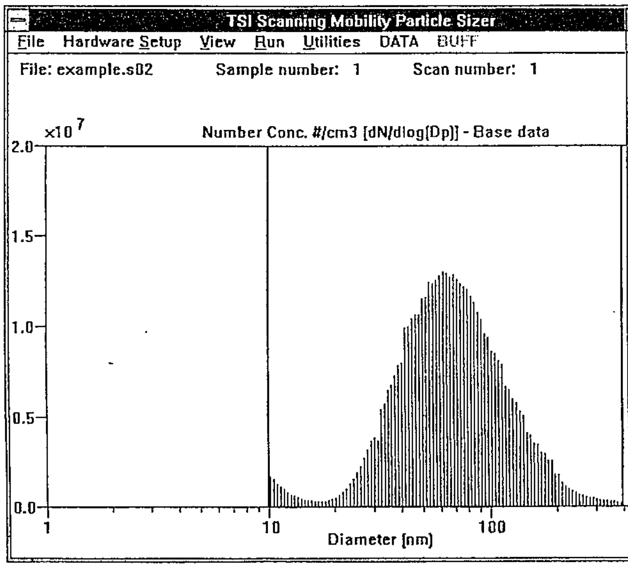
Influence of SMPS Scan Times



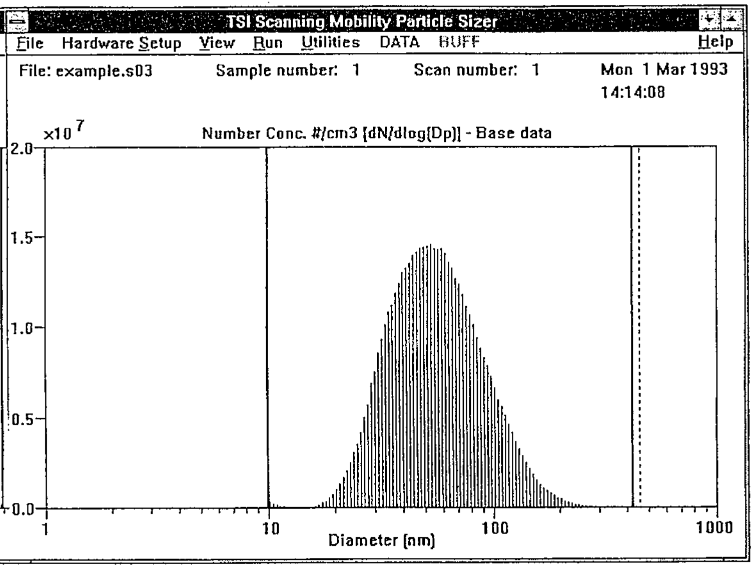
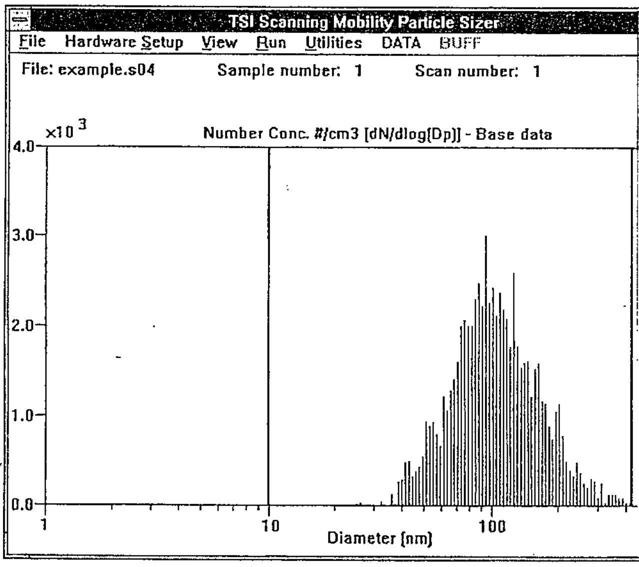


Figure F-2 High particle conc.; SMPS-C 60 s up & 30 s down scan *Steps in distribution result of 3022's photometric mode, updates only once / s*	Figure F-3 Same aerosol & SMPS-C 300 s up & 100 s down scan *Notching effect & also "tail left of 20 nm" reduced (increased down scan time)*

Multiple Scans to Improve Statistics



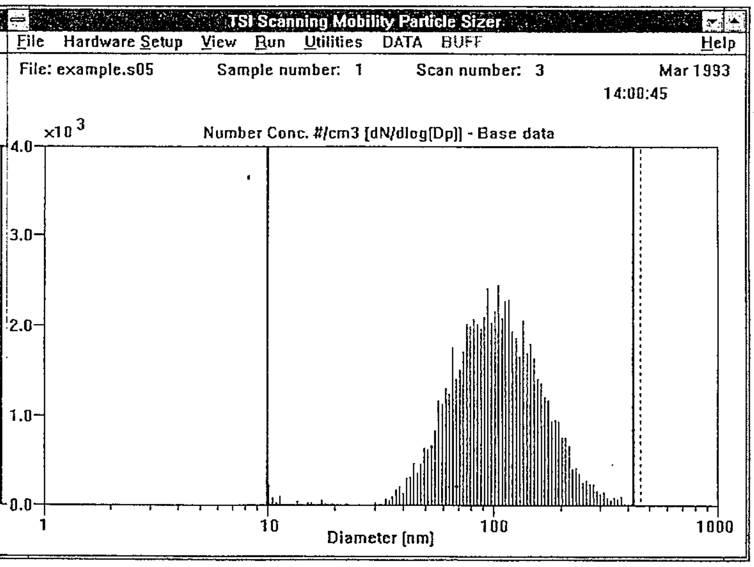


Figure F-4 Low conc. aerosol (N= 1,000 P/cc) SMPS-L *Distribution shows discrete nature of particles detected*	Figure F-5 Same low-conc. aerosol (N= 1,000 P/cc) SMPS-L *Increasing of number of scans per sample from 1 to 3 "smoothes" dist.*

General Measurement Conditions

- Sampling system
  - probe head (geometry & position)
  - sampling lines (short, straight, conductive, heated)
    - transport losses
- dilution
  - avoids condensation (decrease saturation ratio)
  - reduces particle number
  - prevents particle agglomeration; "representative" of real world
  - cools aerosol to be measured

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Summary

- SMPS is valuable tool for nanoparticle studies
  - size range 5 to 1,000 nm
  - high resolution: allows even "nucleation bursts"
  - limitations for dynamic meas. & below 10 nm
  - soon: nano-DMA
    - optimized for range 3 to 50 nm!, low losses
- SMPS: well characterized
- Systematic & statistical errors can be minimized
- Accuracy: total random uncertainty for 0.1 µm PSL is 0.00055 µm (NIST)!

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