Particle Instruments

Characterization of Airborne NanoParticles:

A Short Survey on Aerosol Measurement Techniques

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Electrical mobility & number concentration analysis for aerosol particles

Retired from & Consultant to TSI Incorporated

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Aerosol Particle Characterization

Nanoparticle Parameters to Characterize:

- **Concentration – many choices available**
- **Size distribution – several choices available**
- **Composition – little available**
- **Shape – little available**
- **Surface character – little available - NSAM**
- **Index of refraction – nothing available**
- **Nucleation potential – little available**
- **Others**

Aerosol Particle Characterization

- **We learned yesterday about powder measuring instruments**
- **Airborne particles carry**
  - **A characteristic powder particles don't have:**

-- Concentration --

- **How many particles in a volume of gas?**
- **Usually, particles per cubic centimeter**

Aerosol Particle Characterization

We will first consider

aerosol concentration measuring instruments.

Aerosol sizing instruments measure:

- **– particles per cubic centimeter**
- **– within each of a number of size ranges**
- **– sizing instruments contain a concentration measurement device.**

- **Aerosol is defined as solid and/or liquid particles suspended in gas. Both particles & gas are included in the word ‘AEROSOL’.**

Condensation Particle Counters

Measure number concentration of particles in real time

- **How do CPCs work?**
  - **They make nanometer-sized particles bigger!**
  - **Original name, CNC (Condensation Nucleus Counter), comes from cloud physics where condensation nuclei are precursors to raindrops.**
- **CPC principle has 3 steps:**
  1. **Supersaturated vapor formed from working fluid.**
  2. **Vapor condenses on particles that act as nuclei, forming much larger droplets (1 – 10 μm diameter).**
  3. **CPC optics detect and count particles passing the sensor.**

Ultrafine CPC (UCPC)

- **Top-of-the-line alcohol-based CPC**
  - **Able to detect particles smaller than any other butanol CPC**
  - **Uses sheath air to confine particles to centerline of condenser tube where supersaturation is highest**
- **Initially designed at U of MN as the first scientific CPC for "very, very small" particles**
  - **Lower detection limit slightly smaller than 2.5 nm**
  - **Steep drop-off of smallest-particle detection efficiency**
  - **Fastest response to concentration changes (T_{95} < 0.8 sec)**

Stolzenburg, M.R., and McMurry, P.H. (1991). An Ultrafine Aerosol Condensation Nucleus Counter, Aerosol Science & Technology 14:48-65.

CPC Application Examples

- Vehicle emission testing
- Aerosol & nanoparticle research
- Environmental air quality
- Atmospheric & climate studies
- Filter efficiency testing
- Aerosol transport studies
- Inhalation toxicology
- Respirator fit testing
- Clean air and gas monitoring
- Industrial hygiene investigations

CPC Calibration

ISO 27891 currently under development;

- **ISO TC24 / SC4 / WG12**
- **Next meeting: 3PM *TODAY!***
- **Room Krakau, just one floor below this room**

The method: comparison of concentration with

an aerosol electrometer that is calibrated traceable to national standards.

Liu, B.Y.H., and Pui, D.Y.H. (1974). A submicron aerosol standard and the primary, absolute calibration of the condensation nuclei counter, J. Colloid Interface Sci., 47:155-171.

CPC Availability

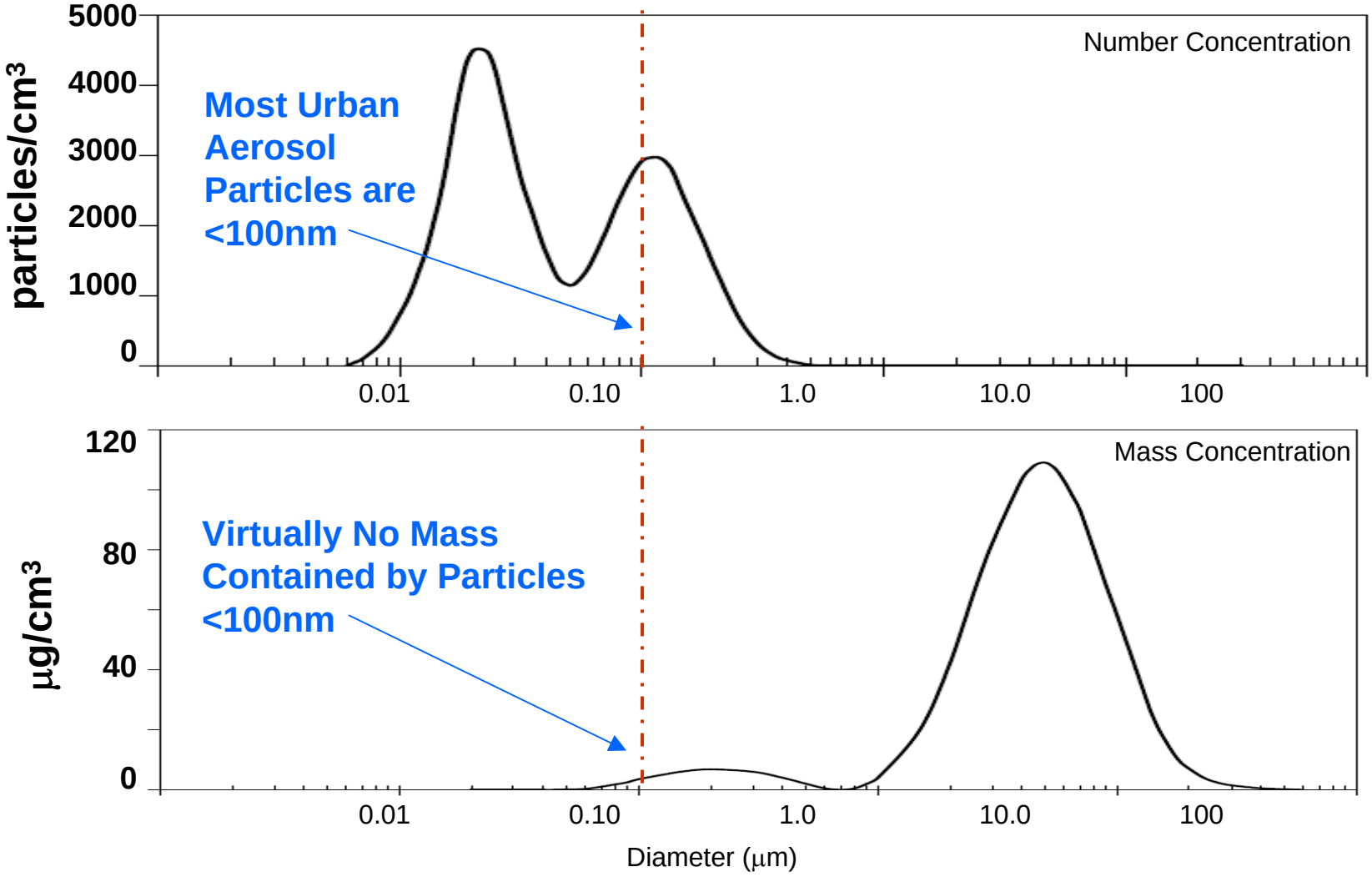
- **CPC models currently available from at least 5 companies from 4 countries:**
  - **TSI, USA**
  - **Grimm, Germany**
  - **Kanomax, Japan**
  - **HCT, Korea**
  - **Horiba, Japan**
- **TSI currently carries at least 10 CPC models.**

What Are Ultrafine Particles?

- **Particles < 100 nm in diameter (definition US EPA)**
  - **UFPs occur in very large numbers in urban air**
  - **Most common source in urban environment are combustion processes (vehicle exhaust in particular)**
    - **UFPs are responsible for nearly all urban smog**
- **Traditional mass measurements like PM_{10} and $PM_{2.5}$ do NOT represent UFPs because UFPs have almost no measurable mass**
  - **It takes one million UFPs (of 10 nm) to equal the same mass of one single 1 micrometer particle.**
  - **Number of coarse (PM_{10}) particles in air pollution is at least 1000x lower than UFPs, yet are majority of mass.**

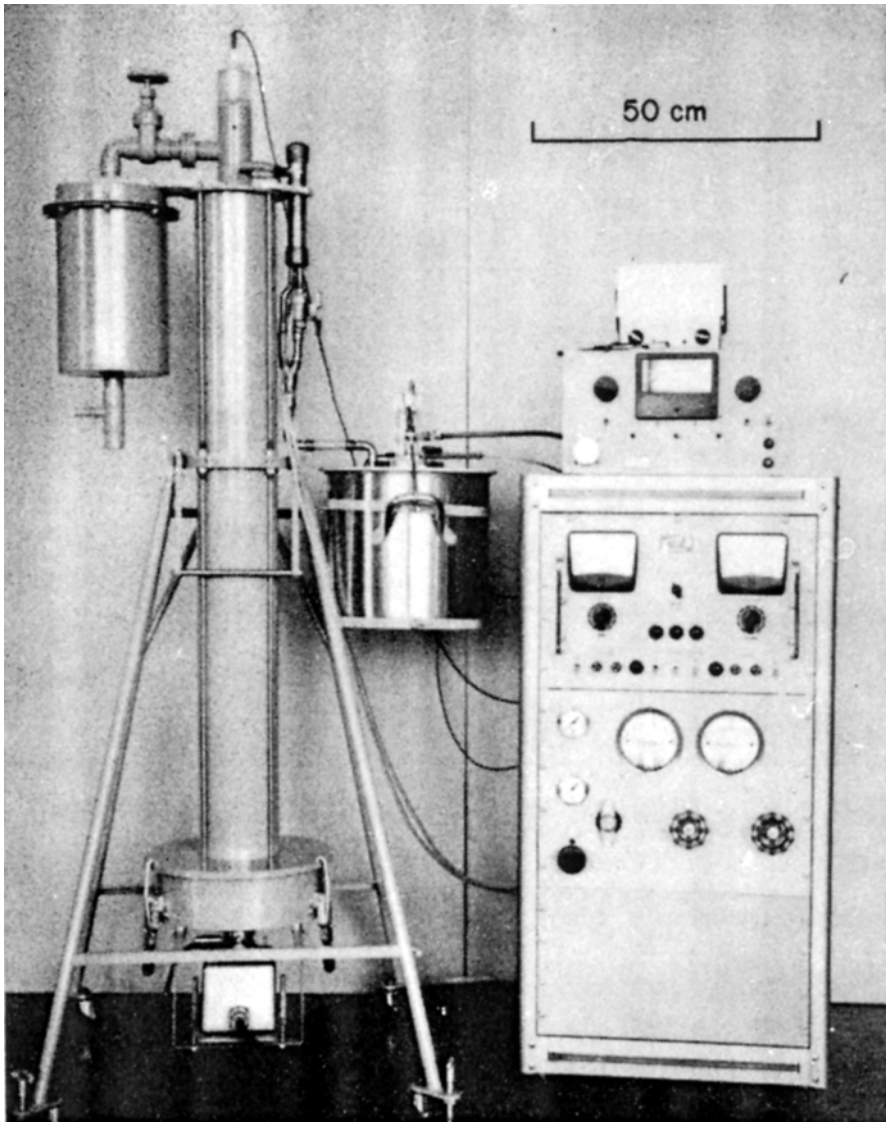
Typical UFP Size Distribution

Typical Particle Size Distribution in Urban Air



Adapted from: Seinfeld and Pandis (1998) Wiley Interscience

How Do We Measure Particle Size Distributions Below 100nm?



Prototype, Whitby Aerosol Analyzer, 1966, © University of Minnesota, development engineer: Gilmore J. Sem

Scanning Mobility Particle Sizer

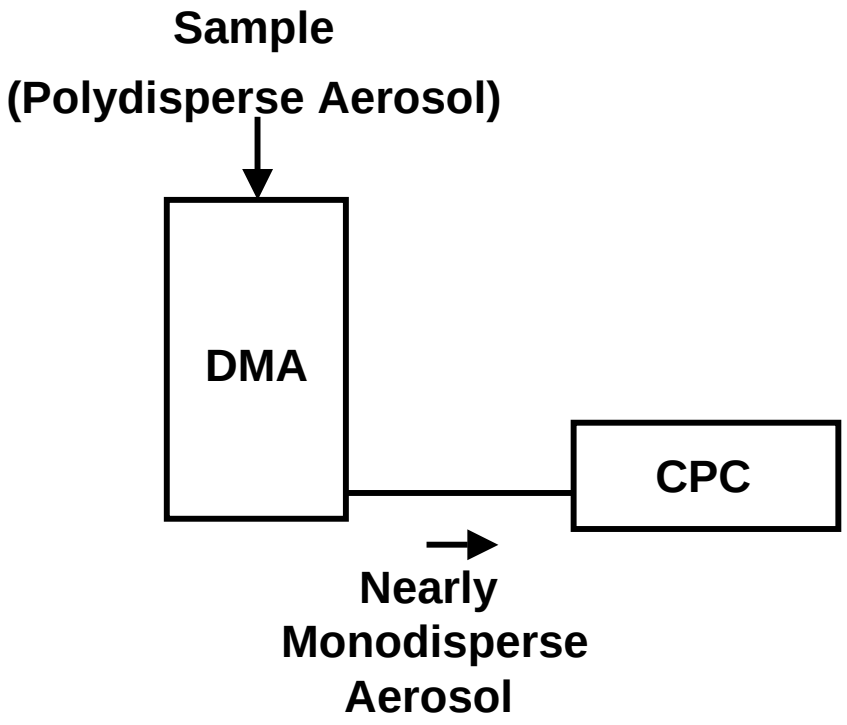
Measures particle size distributions, high resolution

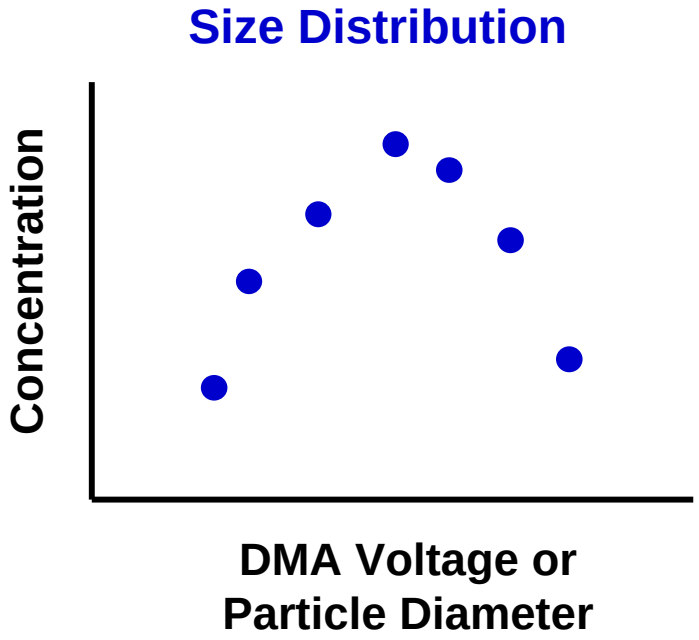
- **Condensation Particle Counters (CPC's) are great detectors of nanoparticles – but they offer no information about particle size**
  - **The use of a Differential Mobility Analyzer (DMA) in front of the CPC allows a narrow size band of particles to first be selected, then fed to the inlet of the CPC to be counted.**
  - **DMA uses the particles' electrical mobility to determine size.**
- **Combination of a DMA and a CPC by a fast-scanning mode of measurement makes it a Scanning Mobility Particle Sizer™ (SMPS™)**

Scanning Mobility Particle Sizer

- **DMA is a narrow band-pass filter**
  - **selects fraction of airborne particles**
  - **within narrow particle size range**
  - **passes them through DMA exit in aerosol form**

SMPS Operational Principle





Stepping Mode > 20 minutes

Scanning Mode (SMPS™) ~ 1-3 minutes

SMPS Accuracy

- **Detailed study at NIST (USA National Institute of Standards & Technology)**
  - **Assessed accuracy of method**
  - **"Investigated *all physical variables* of the size measurement exactly"**
- **Results: 0.1 µm PSL reference particles:**
  - **Reproducibility, 14 measurements: c_v = 0.2%**

Kinney P.D. et al. (1991) Use of the Electrostatic Classification Method to Size 0.1 µm SRM Particles - A Feasibility Study. J. Res. Nat. Inst. Stand. Technol. 96:147.

ISO Standard 15900-2009

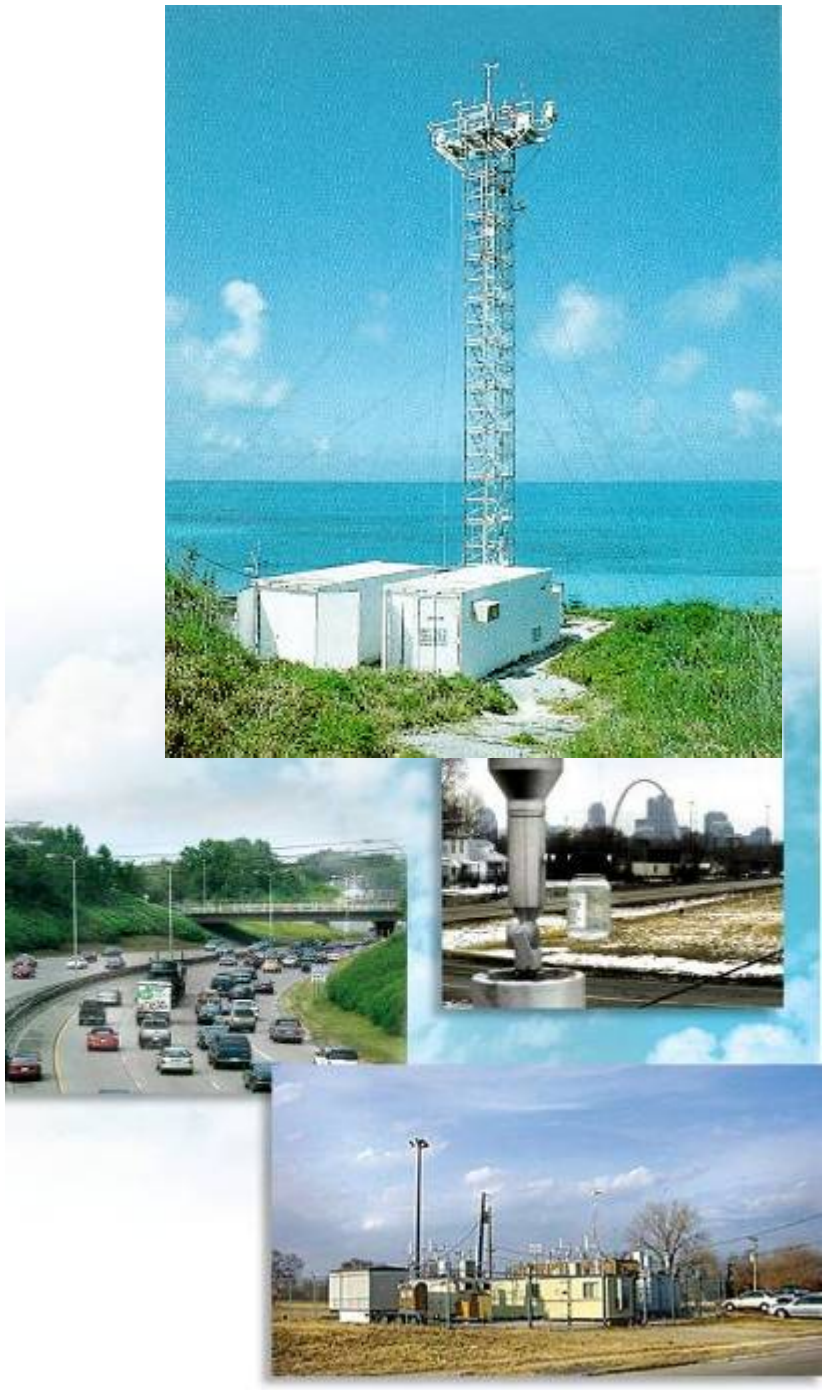
ISO TC24/SC4/WG12 developed a new standard, published 15 May 2009:

ISO 15900-2009

Determination of particle size distribution — Differential electrical mobility analysis for aerosol particles

SMPS Applications

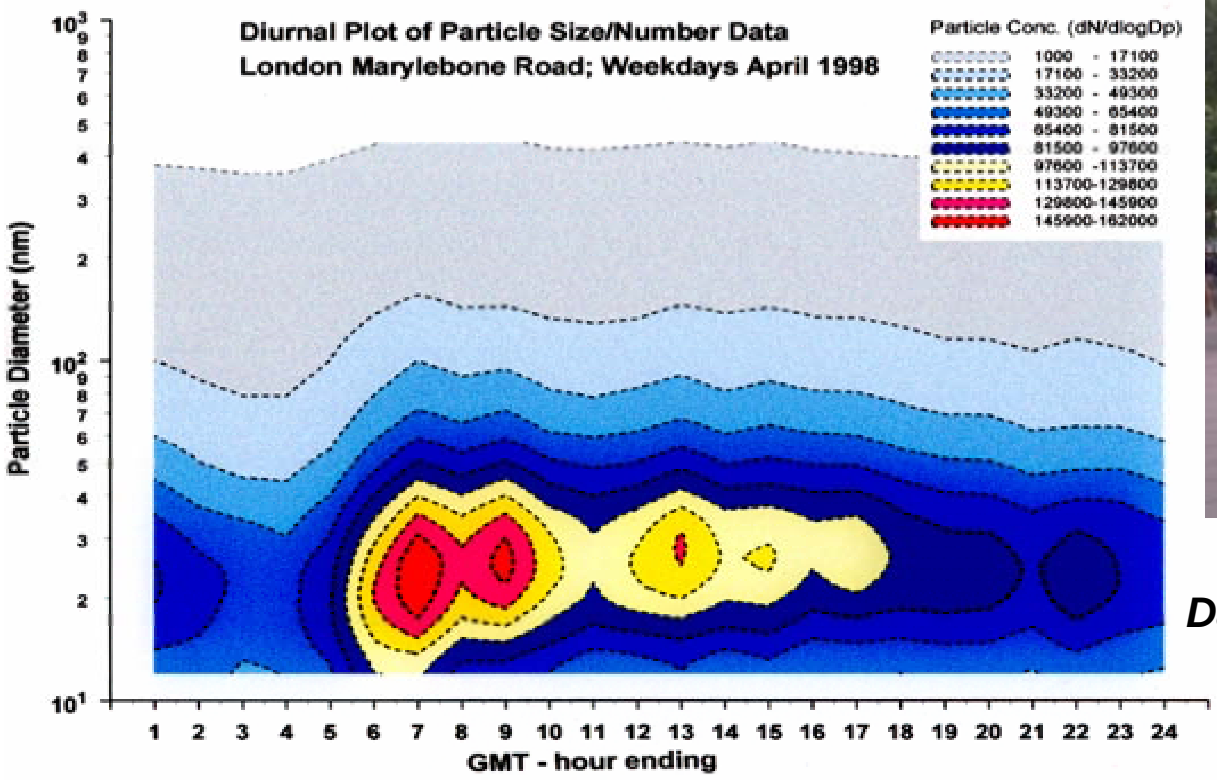
- Basic aerosol research
- Atmospheric & climate research
- Nanoparticle R&D
- Urban air quality
- Mobile studies
- Vehicle emissions
- Combustion research (boilers)
- Ultrafine emissions at workplaces
- Indoor-air-quality measurements
- Laser printer emissions
- Filter efficiency testing
- Tobacco smoke
- Nucleation & growth studies



SMPS Application: Urban Air

Ambient measurements near a busy London road

Diurnal pattern heavily dependent on traffic emissions



Data Courtesy Prof. Roy M. Harrison OBE, University of Birmingham

SMPS: Vehicle Emissions

Particle emission measurements

- Light-duty diesel (cars & vans)
- Heavy-duty diesel (trucks & buses)
- Spark-ignition engines
- Marine diesel (ships)
- Aircraft

- **Exhaust aftertreatment**
  - Characterization of diesel particle filters
- **Development of alternative fuels**
  - Low-sulfur diesel; additives

Chassis Dynanometer Photo Courtesy of Ford Forschungszentrum Aachen

Fast Mobility Particle Sizer

Measure size distributions; fast time resolution

- **SMPS works well for quasi-stable conditions**
  - **Need for similar measurements with faster time resolution**
- **FMPS designed primarily for real-time sizing**
  - **Complete size distribution every 1 second (1 Hz)**
  - **Based on electrical mobility analysis and 20+ years of experience with multiple detectors at U of Tartu, Estonia**
- **Important features**
  - **Electrical mobility technique, similar to SMPS**
  - **Lower detection limit 5.6 nm**
  - **Size resolution: 32 channels total**

Mirme, A.A., Tamm, E.I., and Tammet, H.F. (1981). An aerosol electrogranulometer with a wide measuring range. Acta et comm. Univ. Tartuensis, 588: 84-92. (in Russian, with English abstract)

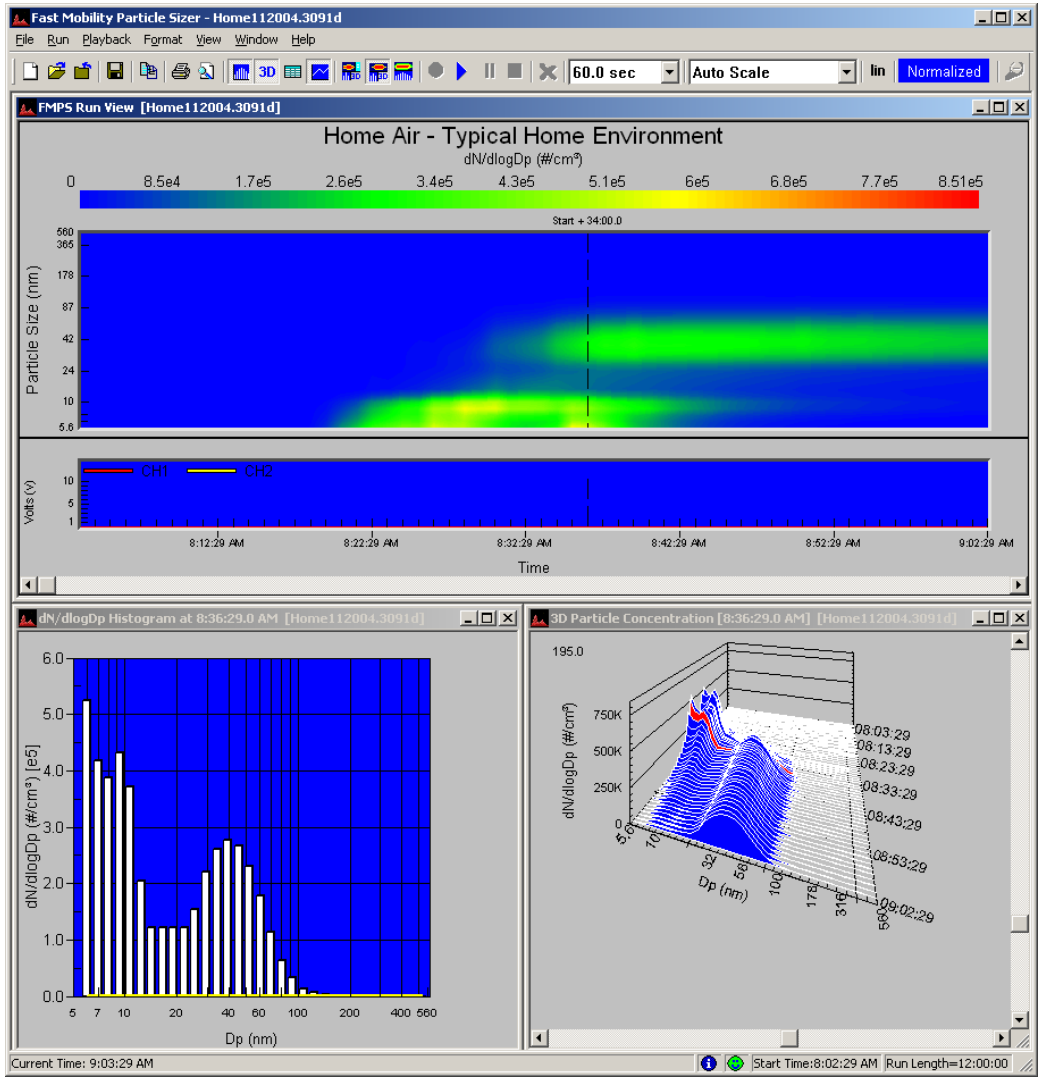
FMPS Application: Gas Burner

Dynamic particle formation events

Initially starts with nucleation, particle diameter < 10nm

Later accumulation mode only, particle diameter ~ 50nm

3-D plot shows changes with 1 sec time resolution



Aerosol Particle Characterization

- **Airborne particles may be solid, liquid, or a mixture of solid and liquid.**
- **The composition and phase of the constituents of a particle are often not uniform throughout the particle or over the surface of the particle.**
- **There is much to learn; many aerosol research instruments not yet invented.**

What Regulatory Activities & Initiatives Are Taking Place?

European Regulatory Activities

- **Recently, European Union established first regulation that focuses on restricting emissions of UFP (ultrafine particles)**
  - **Particle number limit for light duty diesel vehicles, Euro 5/6**
  - **Euro 5 limit: 6×10^{11} particles/km**
- **VDI/DIN's Clean Air Commission is preparing German national guidelines for particle number concentration & size distribution measurements in air quality regulatory monitoring networks.**
- **CEN/TC 264/WG 32 is working on technical recommendations for number concentration and size distribution measurement of UFP in air quality monitoring networks.**
- **California Air Resources Board is closely monitoring European activity and contemplating UFP regulations.**

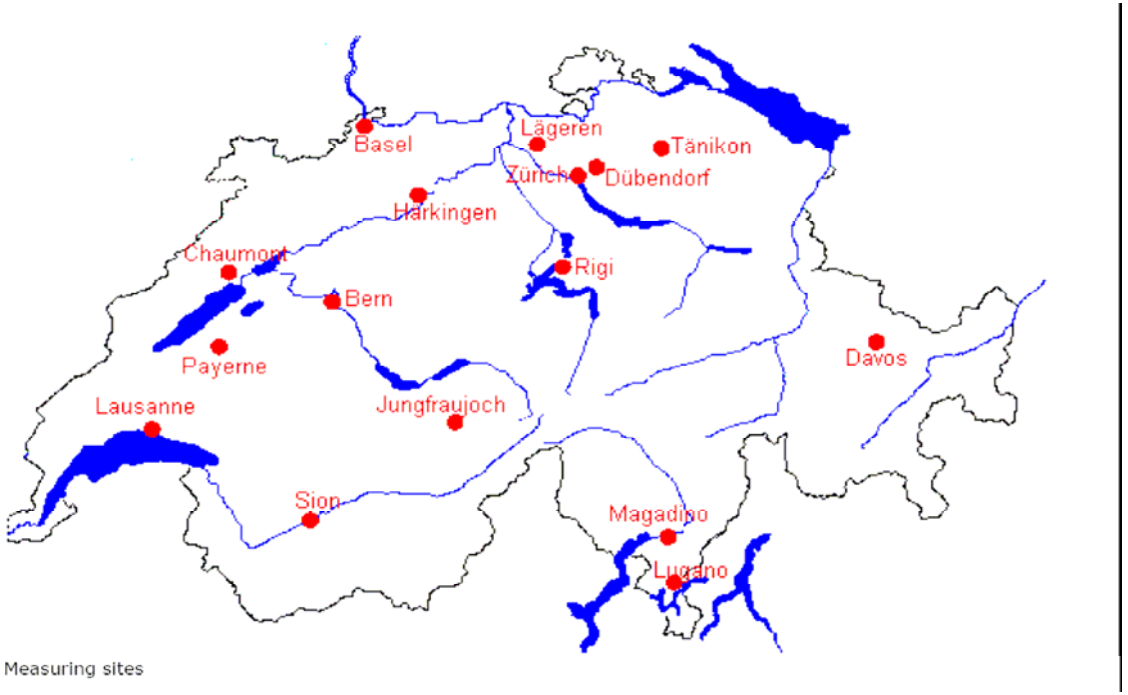
European Initiatives

- **Researchers have recognized importance of UFP measurement for many years (ACE-1, ACE-2, etc.)**
  - **Number concentration and size distribution measurements part of atmospheric research and epidemiology studies**
- **Long-term study in Erfurt by GSF**
- **Since 1998, UK monitoring sites have routinely and continuously measured UFP number concentration and/or size distribution**
  - **Three sites use SMPS for size measurements**
  - **One urban roadside, one urban background, one rural background make 5 scans in 15 minutes**
  - **9 CPCs in cities routinely measure number concentration**

Swiss Initiative

- **From 2001, Switzerland pioneered UFP monitoring in NABEL monitoring stations as part of the MfM-U project**
  - **6 out of 16 stations routinely run CPCs (Model 3022A)**
  - **Data reported online at http://webclientmona.innetag.ch/**

Messstation Härkingen



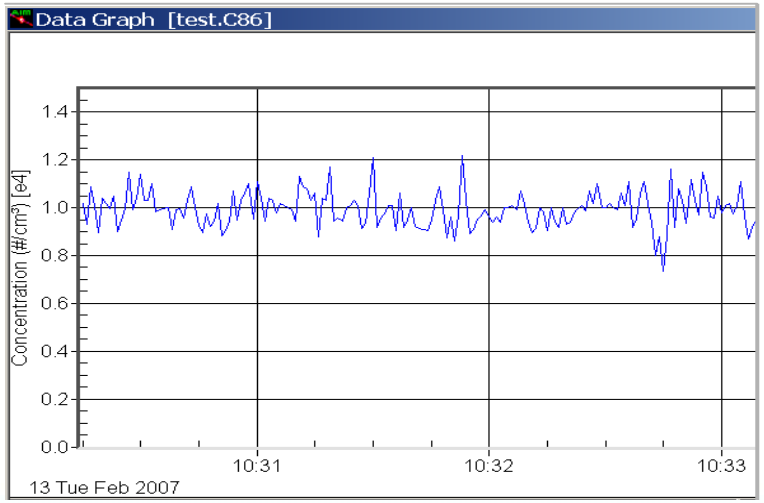
Measuring sites

www.empa.ch/plugin/bean/empa/Article_PrintArticle?pr_artid=13204&wo=1

Environmental Particle Counter 3783

Continuous, accurate measurement of UFP concentrations in real-time

- **Measure particles down to 8 nm (0.008 micron)**
  - **Designed for high concentration environments**
  - **Superior reliability and accurate measurement where FRM and equivalent mass-based methods fall short**
- **Easy to operate, low maintenance & advanced instrument diagnostics**



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UFIPOLNET Project

EU-Life “UFIPOLNET”

- **EU-project; objective to develop new UFP instrument optimized for use in air quality monitoring networks**
  - **Easy integration into routine monitoring systems**
  - **Well suited for continuous monitoring (24 h / 365 days)**
  - **Affordable price**
  - **Low cost of ownership**

- **Four prototypes demonstrated capability during 12 months of continuous operation at 4 routine monitoring sites.**

UFIPOLNET Field Evaluation

Stockholm:
Hornsgatan (street canyon)

Dresden:
Schlesischer Platz (main crossing)

Prague:
Strahovský tunnel (above tunnel exit)

Augsburg:
Friedberger Straße (urban background)

UFP Application: Beijing Olympics

- During bidding process in 2001, Beijing agreed with the IOC to bring air quality within WHO standards
  - On Aug 8 several athletes missed the opening ceremony because they thought the exposure to Beijing air would negatively impact their performance
  - Pollution levels remained a challenge for Olympic Games until the closing ceremony on 24 Aug 2008
- UFP 3031 was used to monitor size-classified particle number concentrations in Beijing during August 2008
  - Measurements supervised by researchers from Cornell and Beijing universities
    - Data will be published separately by these researchers

Environmental Sampling 3031200

Representative sampling and conditioning

- **Quality of measurement can be no better than quality of sample delivered to inlet!**
- **Standard PM_{10} inlet**
  - **Standard size-selective inlet for outdoor aerosol**
- **Sharp cut PM_1 cyclone**
  - **Removes large particles to avoid contamination**
- **Flow splitter**
  - **Splits inlet sample flow to enable sub-sampling a portion of the flow into a particle instrument**
- **Nafion® dryer**
  - **Conditions the sample to remove effects of relative humidity on the sample**

Other Aerosol Nanoparticle Instruments for Research

- **More complex instruments developed for specific research applications:**
  - **Tandem DMA for studying effects of dynamic processes on aerosol nanoparticles, such as relative humidity, gases / vapors, radiation, etc.**
  - **Ehara aerosol particle mass analyzer (Kanomax) to characterize individual airborne nanoparticles by mass-to-charge ratio.**
  - **Particle beam MS (U of MN), Aerosol TOFMS (TSI), Aerosol MS (Aerodyne) for measuring composition of individual aerosol particles.**
  - **Atmospheric ion characterizers, and others.**

Summary

- **Growing need to measure ultrafine & nanoparticles**
  - **Environmental aspects, health risk, nanotechnology, etc.**
- **Current mass measurement DOES NOT DETECT UFP**
  - **Measurement of nano-sized particles is best based on number counting methods due to high number & little mass**
- **As particle research instruments move to continuous monitoring and industrial process applications, internationally recognized standards are important.**
- **There is need for many more instruments to measure important aerosol characteristics that cannot yet be measured.**

Note of Appreciation

- **About half my visual powerpoint images came from Oliver Bischof of TSI's Aachen office.**
- **Thank you, Oliver, for your inspiring material!**
- **Thank YOU for attending this workshop!**