Instrumentation for Ambient Ultrafine Particle Measurement

historic perspectives and recent developments

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Ultrafine Particles Dominate Particle Number Concentrations

Rural and Urban Sites: Similar Relationship between Ultrafine Particle Number Concentrations and Total Particle Number Concentrations
Simplest Indicator for Ultrafine Particles:

Particle **Number** Concentration

_Bricard et al, 1976_  
_Hering et al, 2005_
1889: First Measurement of Atmospheric Particle Number Concentrations

John Aitken,

“On the Number of Dust Particles in the Atmosphere”,

Transactions of the Royal Society of Edinburgh, 1889
How Aitken’s Instrument Worked

- Humidified air sample
- Expanded adiabatically
- Droplets formed around particles, which then settled
- Counted manually
- Repeated with dilution

Receiving flask into which sample is expanded, with counting stage

Sample collection flask

Filter
The reason of the greater number of particles in the room than that found outside was due to the particles produced by the two gas flames burning in the room at the time.
• **1912: Wilson Cloud Chamber**
  - 1929: Nobel Prize for particle physics
  - Determined precise expansion ratios for avoiding homogeneous and ion-induced nucleation of particles

• **1930s: Scholz:** Automated expansion for particle counting

• **1950s: Vonnegut:** Automated counting by recognizing particles grow to uniform size.
1950s: Vonnegut, Automated Counting

Automated, but not continuous
( condensing vapor: water )
1970s: Thermally Diffusive Condensation Particle Counter (CPC)

Automated & Continuous (condensing vapor: butanol or other alcohol)
Widely used, suitable as detector for size distribution instruments
Many models, sold by several companies

Bricard et al, 1976
Can you have a Continuous, Automated Particle Counter without Butanol?

- **Challenge**: too small for direct optical detection
- **Approach**: Create region of supersaturation to activate particle growth => form droplets
- **Why Supersaturation?** Equilibrium vapor pressure over a droplet is greater than over a flat surface due to free energy associated with surface (surface tension)
- **Kelvin Relation**:  
  \[ P_{\text{droplet}} = P_{\text{flat surface}} \exp\left( \frac{2 \sigma v}{kT \rho R} \right) \]  
  - Surface tension
  - Particle radius
Thermally Diffusive CPCs: Operational Principle

- Saturate flow with vapor
- Flow into cold-walled tube
- Vapor condenses on particles
- Requires slowly diffusing vapor (e.g. butanol)

Saturator, 35°C  Condenser, 10°C  Optics Head

Thermal Diffusivity,
air = 0.215 cm²/s
Mass Diffusivity,
butanol = 0.081 cm²/s

Note: diffusivity of water = 0.265 cm²/s > air
Does not work well with water
2003: Water Condensation Particle Counter (WCPC)

- **Cold** flow enters **warm** wet-walled tube
- Water vapor diffuses more quickly than flow warms
- Supersaturation, particle activation and growth occurs inside of a warm, wet walled tube.

![Diagram of WCPC process]

2003 WCPC (~5 nm) : Saturator, 20C  Condenser, 60C
2004: Saturator, 12C  Condenser, 75C
Nano-WCPC (~2.5 nm)

Thermal Diffusivity,
air = 0.215 cm²/s
Mass Diffusivity,
water = 0.265 cm²/s
Comparison of Centerline Water Saturation Ratios

WCPC: Inlet flow at 20°C & 100%RH, Wetted walls at 60°C
Traditional: Inlet flow 60°C & 100%RH Wetted walls at 20°C
Water Condensation Particle Counter

Hering et al, 2005
First laminar-flow WCPC Response to Ambient Aerosols & Vehicle Emissions

Tunnel Measurements with Antonio Miguel, Arantza Eiguren-Fernandez, UCLA

Detection Efficiency vs. Particle Diameter (nm) for TSI-3785

- Blue dots: Ambient Aerosol (Berkeley, CA)
- Brown dots: Vehicle Tunnel Aerosol (Caldecott)
Calculated Supersaturation Profiles within the Ultrafine Water – CPC

$\mu_v = \pi \alpha_v z/Q$

$\alpha_v$ = vapor mass diffusivity
$z$ = axial distance
$Q$ = volumetric flow rate
Calibration of the Ultrafine WCPC Water Residue Particles

Efficiency for TSI-3786 (water residue particles)

- Positively Charged Particles
  - \( D_{50} = 2.4 \text{ nm} \)
- Negatively Charged Particles
  - \( D_{50} = 2.1 \text{ nm} \)

TSI-3786
Comparison of Water CPC and TSI Ultrafine, Queen’s College, NY (Univ. at Albany, EPA Supersite)

Ambient air inlet

Size-Selection by Electrical Mobility

Filtered room air

0.6 lpm

1.5 lpm

1 lpm

TSI 3025 (ultrafine)

WCPC (TSI 3785)

Compare:
0.2-sec average
11-sec running average

counts/cm³ measured below nanoSMPS
(not ambient size distribution – no charging correction)
Comparison to Butanol Ultrafine CPC with Nano-DMA

Particle counts per 0.2 sec window (average over two scans)

TSI-3025: 1.1±1.0 particles (0.5cc/s)
WCPC: 35 ± 6 particles (16.7 cc/s) --- much better counting statistics

In collaboration with ASRC, University at Albany
Field Comparisons Among CPCs
Total Particle Number Concentrations for Traffic Emissions

Ultrafine WCPC (TSI-3786) compared to Butanol UCPC (TSI-3025)
Ambient Sampling In Riverside, California
Ultrafine WCPC – 3786 & Butanol UCPC - 3025

Riverside SOAR - ICAT

- Water CPC TSI-3786
- Butanol CPC T3025

One-Minute Data
One-to-One Line
slope=1.065, R=0.993
2005: Micro-Environmental WCPC

Size: 7” x 7” x 5”

Weight: 5 lb

Power 12 V, 30 Watts

Features:

- Internal data logging
- One week unattended
- Up to $10^6$ particles/cm$^3$
- In single count mode
Response to Near-Monodisperse Aerosols

MICRO-ENVIRONMENTAL Water-CPC

DMA-Selected Aerosol, 10/15/05
10% mobility window with TSI "long" DMA
Reference: TSI-3025 Butanol Ultrafine CPC/Eff

- Green triangles: Freeway-influenced Ambient (Berkeley)
- Blue circles: Isopropanol Residue

TSI-3781 prototype
ME-WCPC Measurements in a Residential Kitchen

- Residential Kitchen
  - Butanol CPCs
    - T3025
    - T3022
- Water CPCs
  - T3786
  - QME2
  - QME3
  - T3785_Calc

Oven on at 6:05 pm
Summary

• 1890’s
  Aitken, first explorations of airborne particles number concentration
  Identified combustion as source of particles

• 1920s-1950s
  Advances on Aitken’s approach: automated instruments

• 1970’s
  First continuous flow condensation particle counters
  widely used, especially as detectors for mobility size distributions

• 2003
  Introduction of continuous water-based condensation counters
Acknowledgements

- California Air Resources Board, who provided funding for many of the field comparisons.

- ASRC, University at Albany and the EPA Supersites Program who made possible the measurements in New York City.

- TSI Inc., who loaned equipment for our field and laboratory testing.

- Quant Technologies LLC, who provided the engineering and detailed instrument design.