

Primary Standard for Aerosol Particle Number Concentration

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11th ETH Conference on Combustion Generated Nanoparticles

August 12, 2007

Introduction

Development of the Japanese primary standard began in 2004 at AIST.

Motivations

- Maturity of aerosol measurement instrumentation
- Long-standing scientific interests in CPC characteristics
 - Many experiments have been carried out to 'calibrate' the lower detection limit.
 - The absolute accuracy of CPCs has been unknown due to the lack of a common reference standard.
- PMP activities

It is near completion, and the calibration service will begin in October 2007.

Outline

“Primary Standard for Aerosol Particle Number Concentration”

Introduction

The Standard: A Faraday-cup Aerosol Electrometer

Concentration Measurement by the Standard AE and its Uncertainty

Uncertainty Components

Calibration Station

Factors of Calibration Uncertainty

Comparison of the Standard AE with an OPC

Particle Material for Calibration

Conclusions

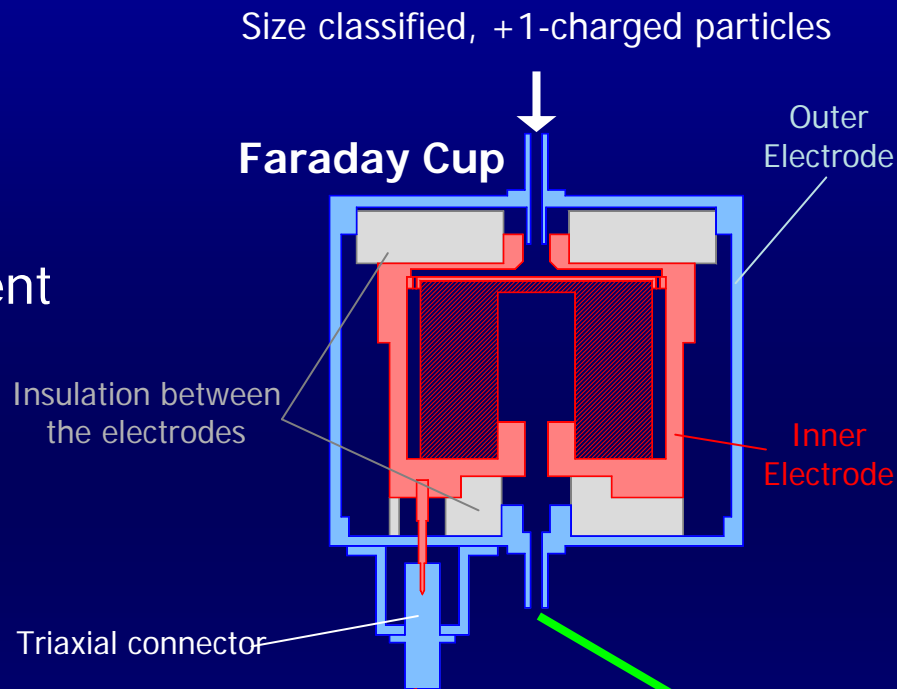
The Standard

- It is a Faraday-cup Aerosol Electrometer (AE).
 - Historically, AEs have been used as an “absolutely accurate”, reference standard in CPC calibrations.
 - Advantages of the Faraday-cup AE
 - Simple
 - Relatively easy to build
 - Robust and stable
 - Analysis of measurement uncertainty is relatively easy.
- Aimed for calibration of CPCs and AEs
 - $10^3 - 10^4$ particles/cm³
 - 10 - 200 nm
 - 1 - 1.5 L/min

The AE

Major components

- Faraday Cup
- Electrometer
- Flow rate measurement and control



Model 6430 Sub-femtoamp
Remote Sourcemeter
(Keithley Instruments, Inc.)



Model DF-240BA
Laminar Flow Meter
(Cosmo Instruments Co. Ltd.)



Model MC-4000
Mass Flow Controller
(Lintec Co. Ltd.)

Flow Control

Concentration Measurement by the Standard AE

$$N = \frac{I}{zeQ\eta}$$

- N Particle number concentration [cm^{-3}]
- I Current [A]
- z Average number of electrical charges on particles [-]
- e Elementary charge (1.602×10^{-19} C)
- Q Sampling flow rate [cm^3/s]
- η "The Faraday-cup efficiency"

"The Faraday-cup efficiency"

- This indicates the degree of non-ideality of the Faraday cup. This value is unity when the Faraday cup works in the ideal manner.
- This is the ratio of the number of particles that reach the inner electrode of the Faraday cup and are detected electrically, to the number of particles that enter the sampling inlet tube of the Faraday cup.
- The non-ideality of the Faraday cup comes mainly from two reasons: filtration efficiency of the particle filter in the Faraday cup being less than 100%, and losses to the inner wall of the sampling inlet tube due to Brownian diffusion of particles.
- The efficiency depends on particle size and sampling flow rate.

Measurement Uncertainty of the Standard AE

The Law of Propagation of Uncertainty

$$u_c^2(N) = \left(\frac{\partial N}{\partial I}\right)^2 u^2(I) + \left(\frac{\partial N}{\partial z}\right)^2 u^2(z) + \left(\frac{\partial N}{\partial e}\right)^2 u^2(e) + \left(\frac{\partial N}{\partial Q}\right)^2 u^2(Q) + \left(\frac{\partial N}{\partial \eta}\right)^2 u^2(\eta)$$

$u_c(N)$

Standard uncertainty of N

$u(I), u(z), u(e), u(Q), u(\eta)$

Standard uncertainty of $I, z, e, Q,$ and η

$\frac{\partial N}{\partial I}, \frac{\partial N}{\partial e}, \frac{\partial N}{\partial z}, \frac{\partial N}{\partial Q}, \frac{\partial N}{\partial \eta}$

Sensitivity coefficient

For our case, the above equation can be written in the following simpler equation"

$$\left(\frac{u_c(N)}{N}\right)^2 = \left(\frac{u(I)}{I}\right)^2 + \left(\frac{u(z)}{z}\right)^2 + \left(\frac{u(e)}{e}\right)^2 + \left(\frac{u(Q)}{Q}\right)^2 + \left(\frac{u(\eta)}{\eta}\right)^2$$

Uncertainty Components (1)

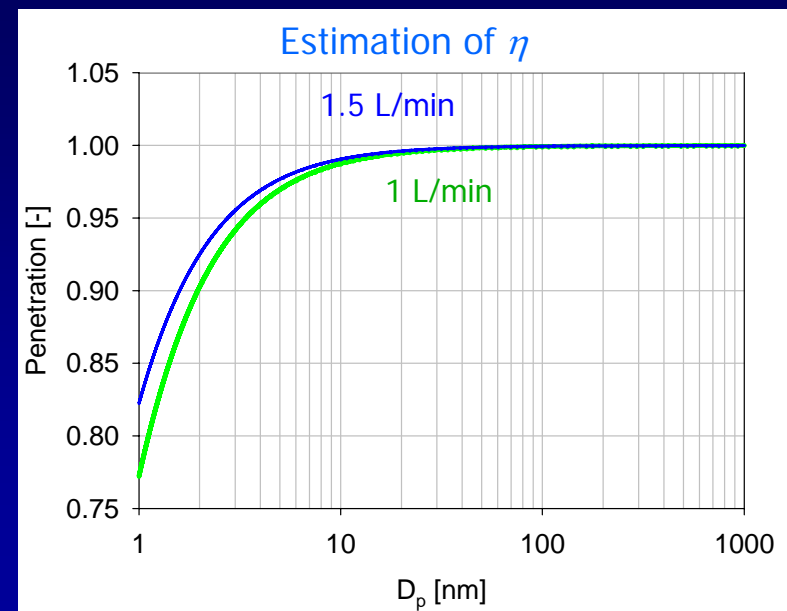
$u(Q)$, $u(e)$, and $u(z)$

- Standard uncertainty of volumetric flow rate Q
 - $u(Q)/Q = 0.0016$
 - Calibrated against standards traceable to AIST (Japanese primary) standards
- Standard uncertainty of elementary charge e
 - $e = 1.602\,176\,487 \times 10^{-19} \text{ C}$
 - $u(e)/e = 2.5 \times 10^{-8}$
- Standard uncertainty of the average number of charges on particles z
 - $z = 1$
 - $u(z)/z = 0.0006$
 - It is expected that contamination by multiply-charged particles is negligible because of the combined use of the electro-spray aerosol generator and differential mobility analyzer (DMA).
 - Estimation of the degree of contamination by doubly-charged particles is experimentally carried out regularly, and the contamination is confirmed to be negligible.

Uncertainty Components (2)

$$u(\eta)$$

- Standard uncertainty of the Faraday-cup efficiency η
 - η = (penetration efficiency by the Gormely-Kennedy equations)
 - $u(\eta)/\eta = 0.12(1 - \eta)$
 - Efficiency of the particle filter in the Faraday cup
 - >99.99% determined by experiment with 100 nm sodium chloride particles
 - The uncertainty is negligibly small.
 - Penetration through the sampling inlet tube against Brownian diffusion losses
 - The length of the sampling inlet tube is 3.5 cm.
 - Estimate by the Gormely-Kennedy equations at 10 nm and 1 L/min is ~1%.
 - The agreement in penetration between the theory and experiment was better than 20%. (Alonso et al., Aerosol Sci. Technol. Vol. 27, p.471 (1997))
 - Other sources of reduction of η ?
 - Compared to a TSI model 3068B AE
 - No significant difference at 4 nm and above.
 - It is unlikely that there are other mechanisms unique to the standard AE that reduce η .



Uncertainty Components (3)

$$u(I)$$

- Standard uncertainty of the current I
 - Calibration against standards traceable to NIST standards
 - Split into two components: systematic $\delta(I)$ and random $\sigma(I)$ terms

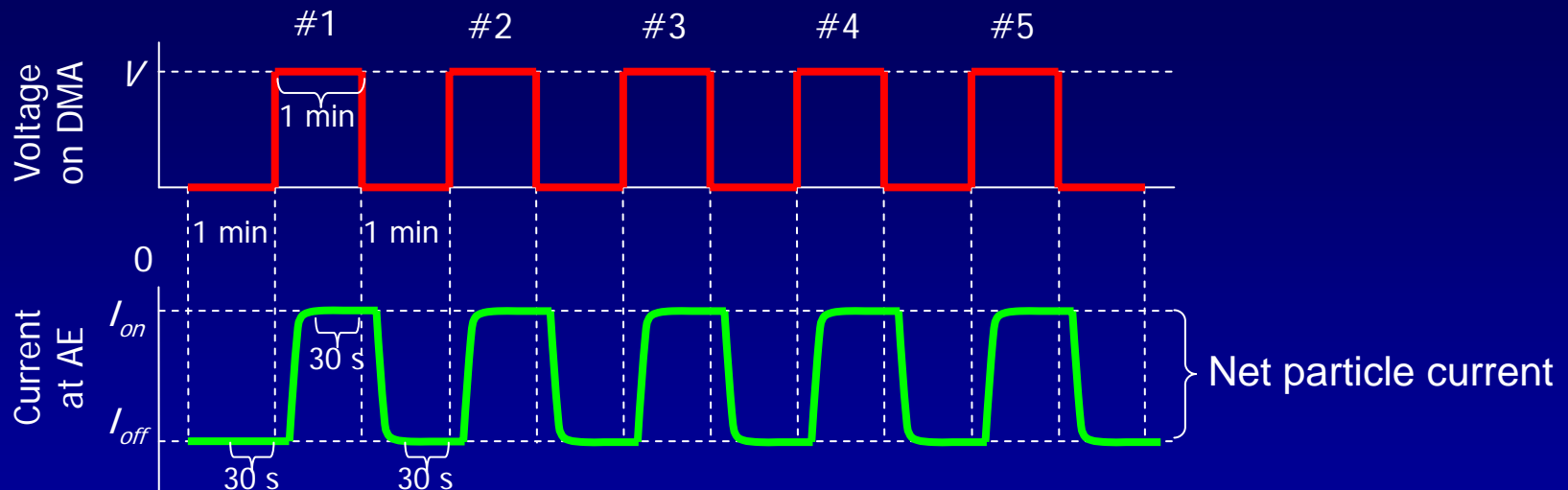
$$u^2(I) = \delta^2(I) + \sigma^2(I)$$

- $u^2(I) = (0.006 I)^2 + (0.10 \text{ fA})^2$ for single measurement
 - The systematic term $\delta(I)$ is determined by the instrument specification and calibration uncertainty.
 - The random term $\sigma(I)$ is determined by experiments.
 - Random dispersions occur in current measurement due to shot noises and fluctuations of the offset current due to variation of the environment temperature.
 - The former can be suppressed by taking the average of repeated measurements, while the latter can be suppressed by reducing the magnitude of the temperature variation.
 - The random term can be reduced by repetition.

$$\sigma(I) = s(\bar{I}) = \frac{s(I_i)}{\sqrt{n}} = \frac{0.10 \text{ fA}}{\sqrt{10}} = 0.03 \text{ fA}$$

Current Measurement

- Measure the net particle current as the difference between the current when the DMA voltage is on (I_{on}) and the current when the DMA voltage is off (I_{off}).
 - The typical time interval is 1 min.
 - To suppress shot noises, the average is taken during each 1-min interval when the reading is constant after the DMA voltage is changed.

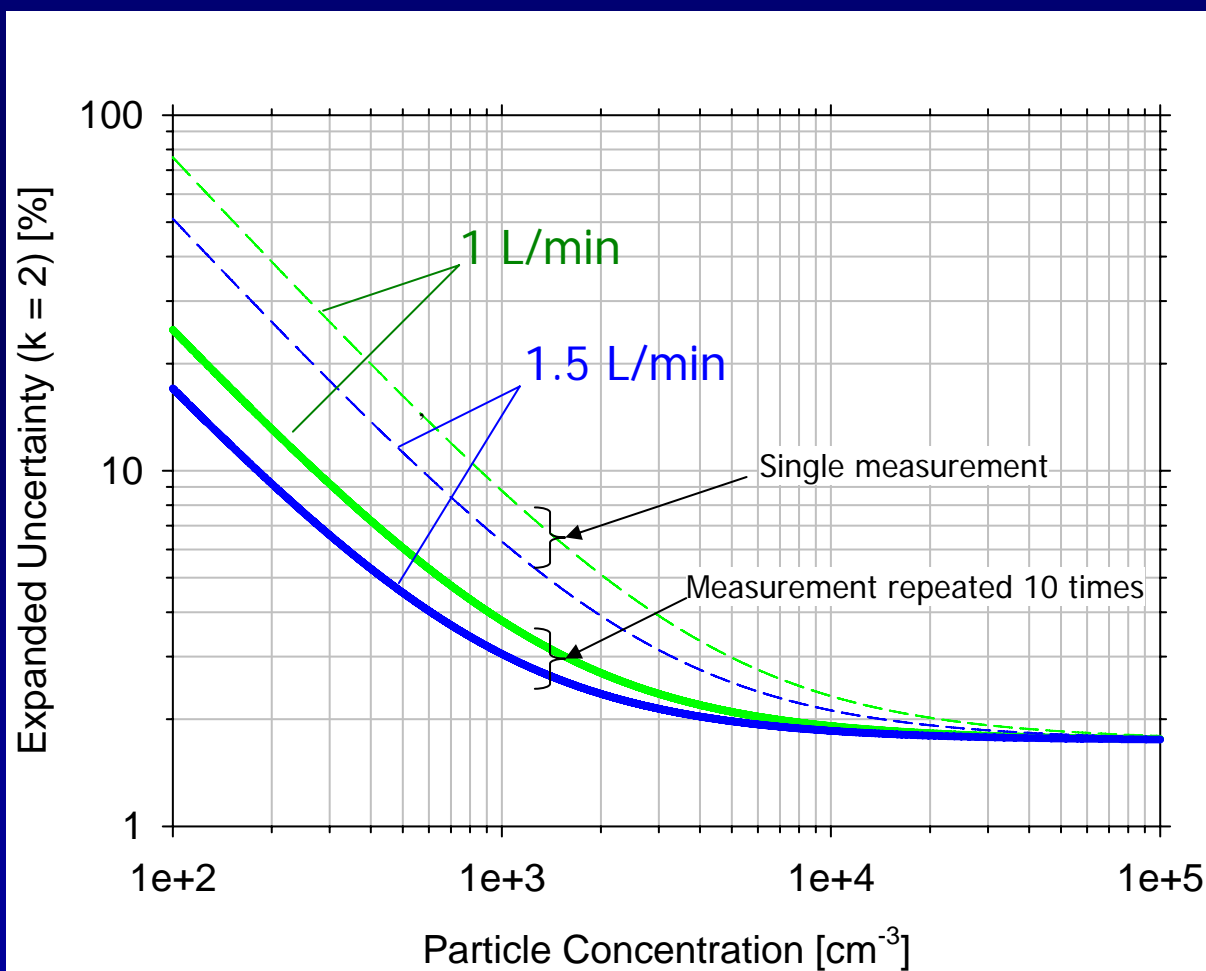


Uncertainty of the Standard AE

Expanded uncertainty of 95 % confidence level ($k = 2$) for 10-nm particles

~2% @ 10^4 cm^{-3}

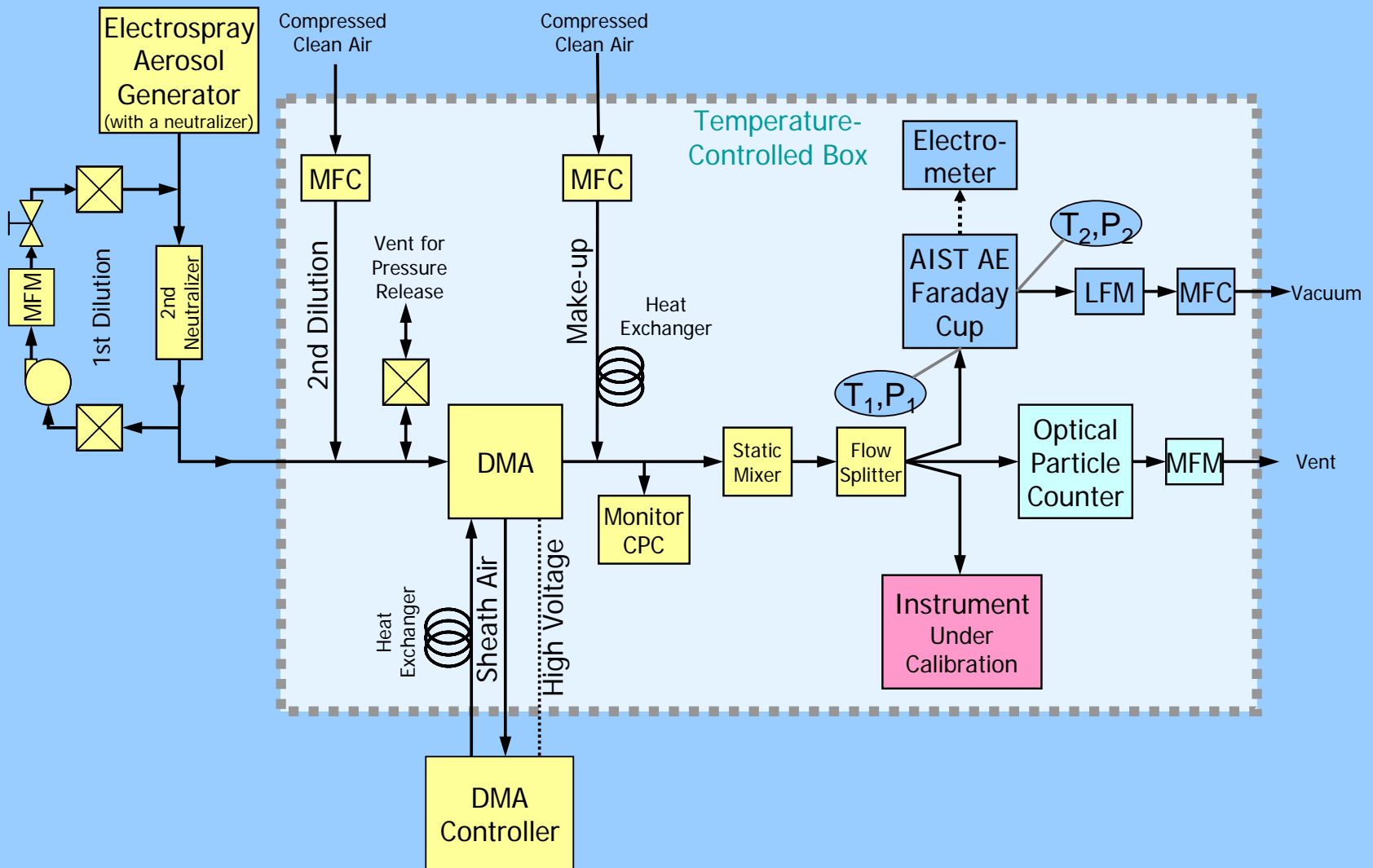
~4% @ 10^3 cm^{-3}

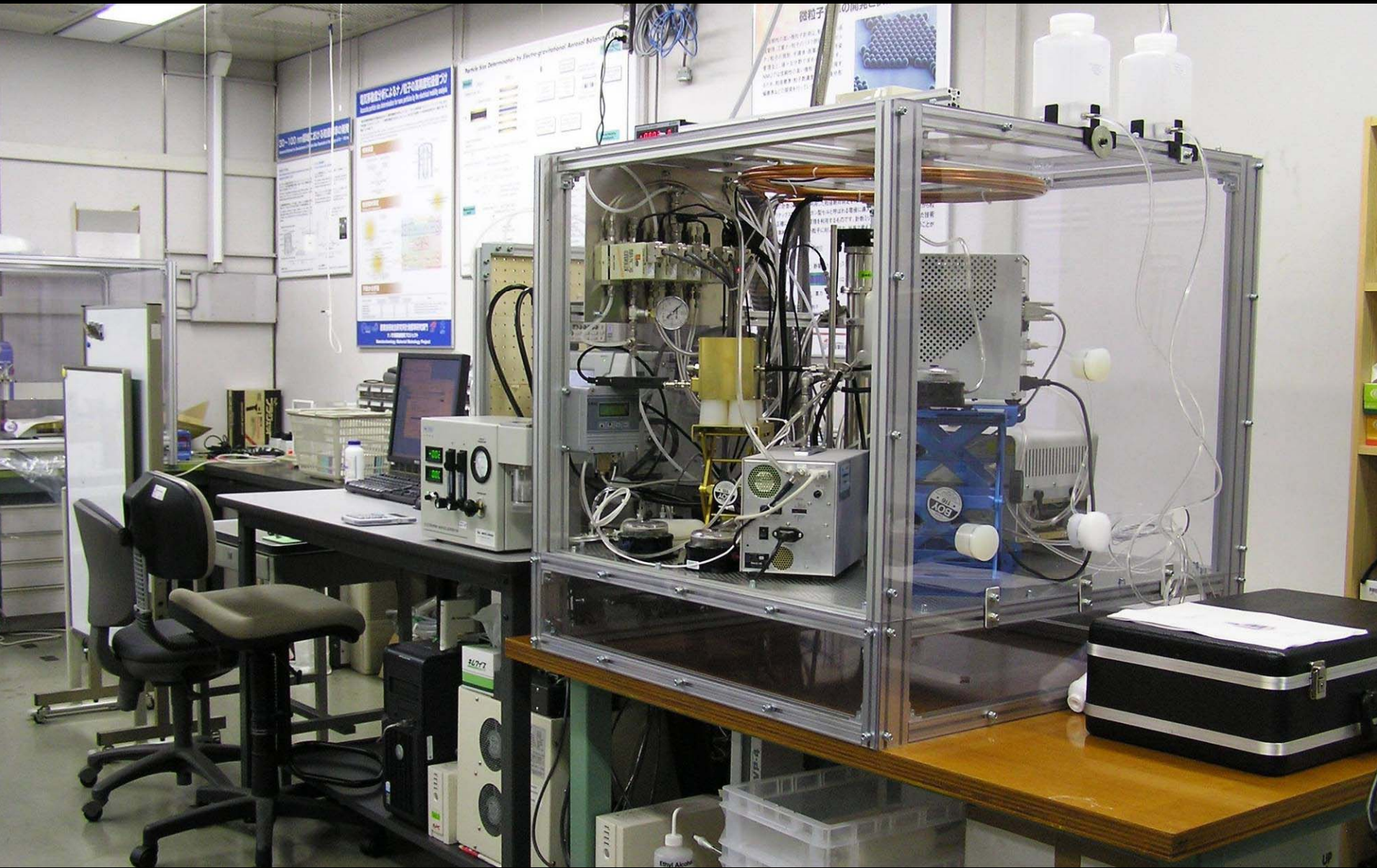


Calibration Station

- Constant-temperature box
 - 90 cm x 90 cm x 90 cm + temperature controller
 - Temperature maintained at about 23°C
 - The variation is within $\pm 0.5^\circ\text{C}$
- Particle generation
 - The electropray aerosol generator (TSI Model 3480)
 - It generates quasi-monodisperse particles at high concentrations in a very stable manner.
 - Concentration downstream of the DMA exceeds 10^4 cm^{-3} for particles of 10 - 200 nm.
 - Particle materials that can be used
 - Sucrose, Santovac[®] oil, PAO (emery oil), Sodium chloride, Ammonium sulfate 10 ~ 30 nm
 - PSL 30 ~ 200 nm
- Size classification by the DMA

Calibration Station





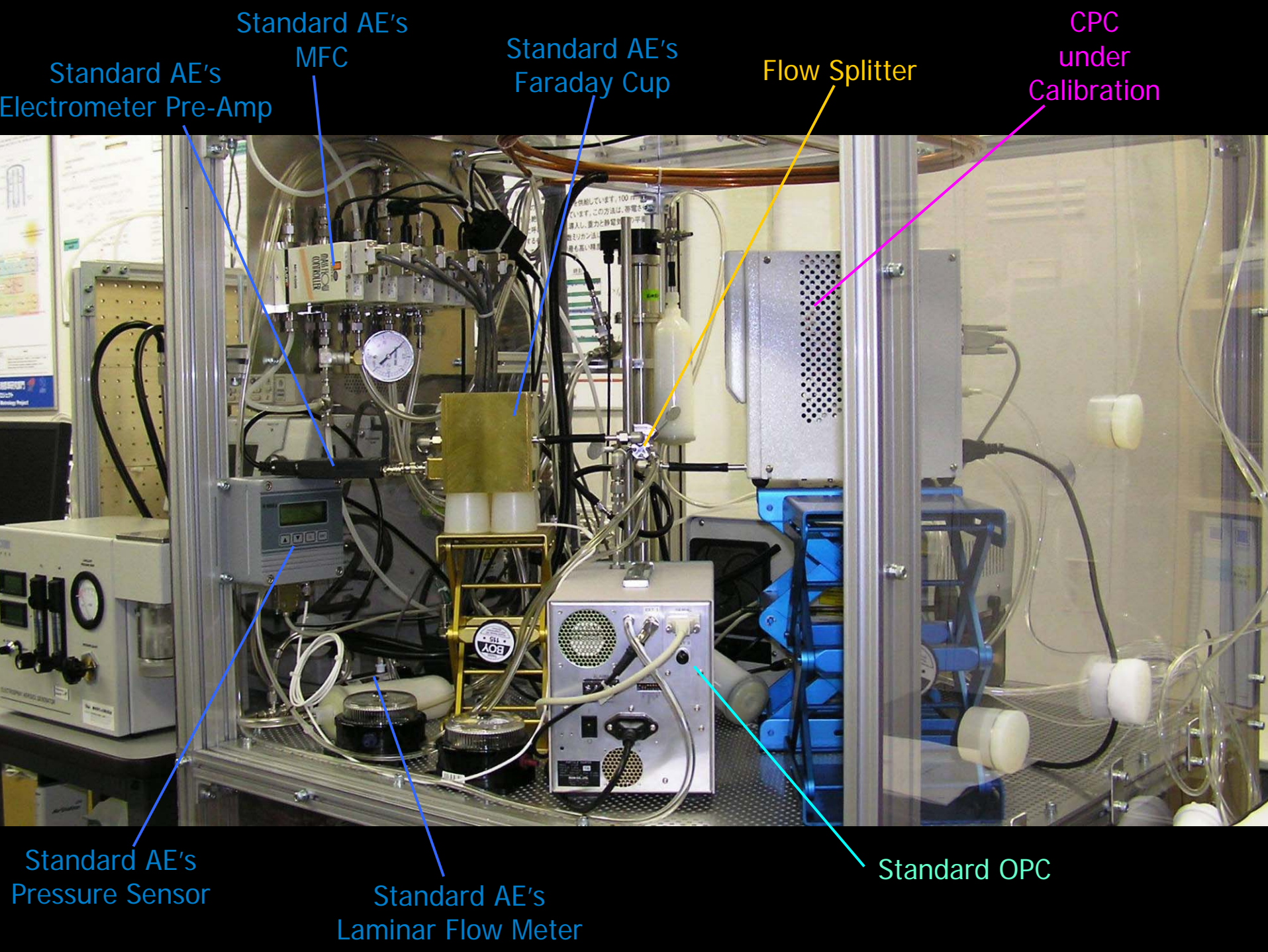
POSTER 1: 2011-2012 Research Report
POSTER 2: Particle Size Determination by Electroacoustic Resonance Balance

微粒子
の測定

100
100

100
100

Equipment Case



Standard AE's
Electrometer Pre-Amp

Standard AE's
MFC

Standard AE's
Faraday Cup

Flow Splitter

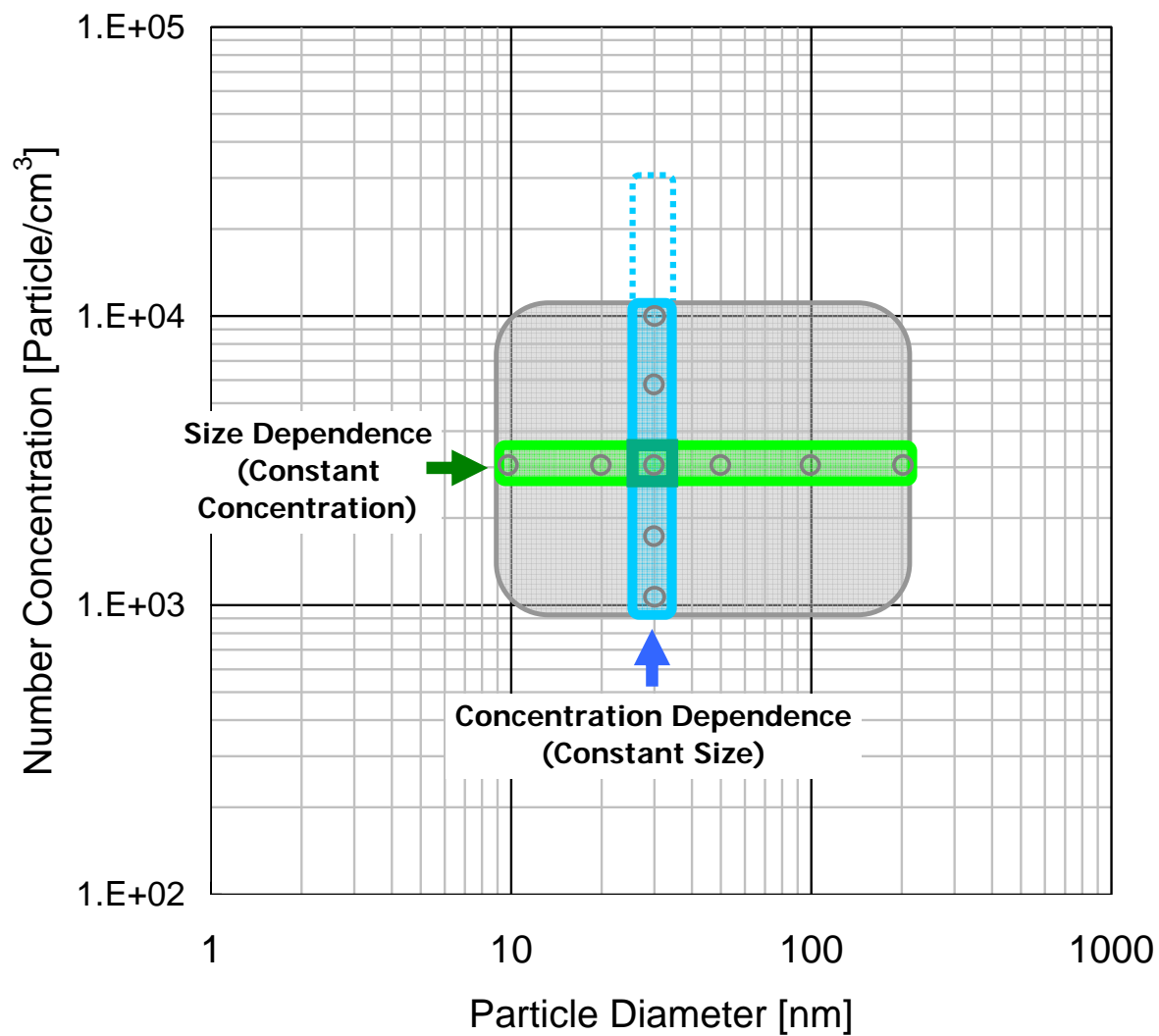
CPC
under
Calibration

Standard AE's
Pressure Sensor

Standard AE's
Laminar Flow Meter

Standard OPC

Calibration Conditions



Other components that may increase uncertainty of calibration results

- Difference in flow splitting ratio
- Difference in losses between the two flow paths
 - These two factors have been already evaluated, and found negligible. (Contribution to the combined uncertainty much less than 0.1%.)
- Error in particle size
 - This is being evaluated.

Comparison with an OPC

Modified Model KC-22B OPC by Rion Co. Ltd.

- Modification was done to increase the maximum concentration (5% coincidence losses) to 10^3 cm^{-3} from the original 10^2 cm^{-3} .
- The flow rate was measured with the LFM of the AE before and after the comparison experiment.
- The comparison was done at 10^3 cm^{-3} with 150-nm PSL particles. Concentrations by the OPC were corrected for coincidence losses.



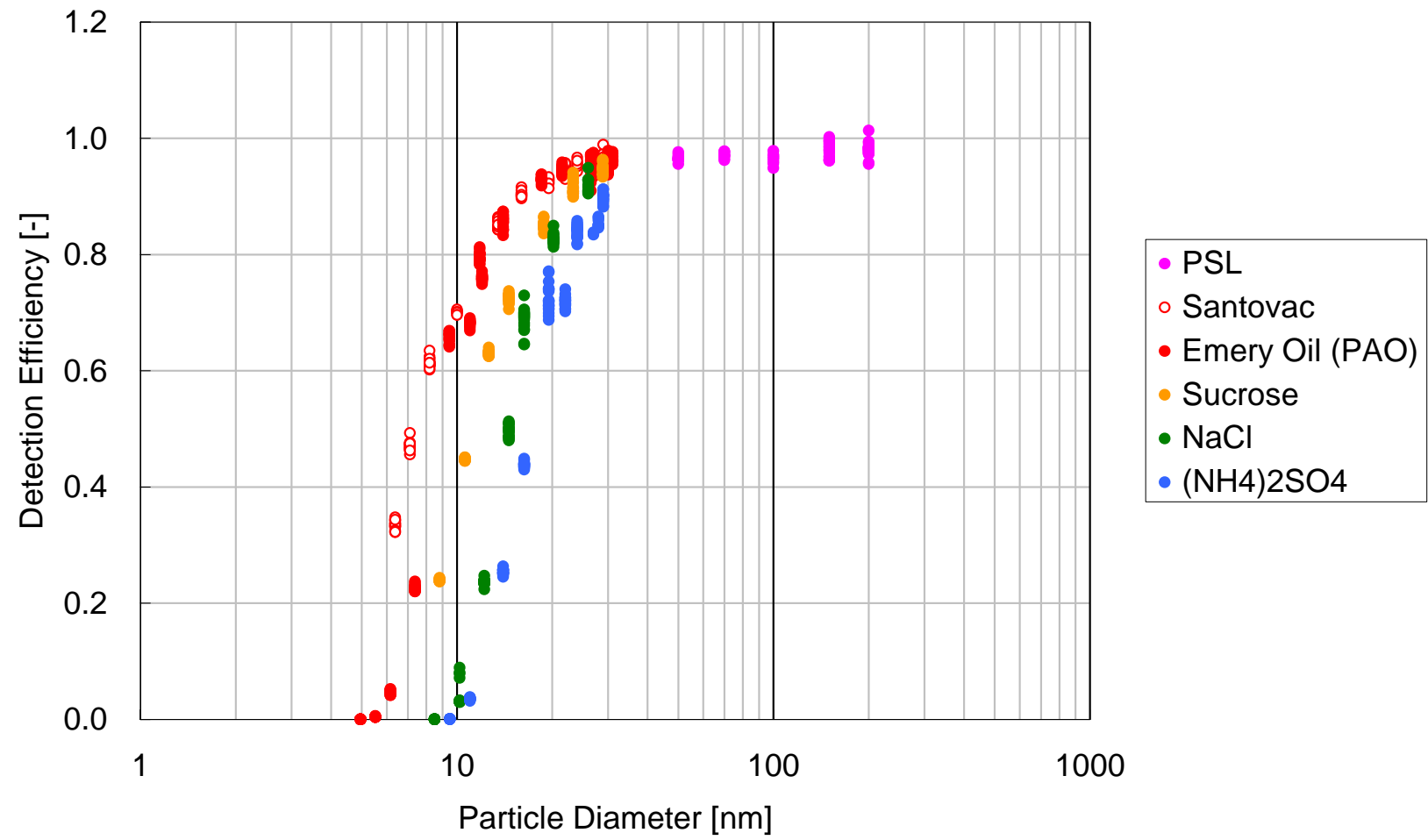
	Day 1	Day 2	Day 3	Day 4
Mean OPC/AE Ratio	0.980	0.995	1.011	1.002
Standard Deviation	0.036	0.036	0.033	0.026
# of Measurements	160	40	140	110
Expanded Uncertainty ($k = 2$)	0.018	0.021	0.018	0.018

Except Day 1, the AE and OPC agreed well with each other within the uncertainty of ~2%.

This suggests that both instruments measure concentration accurately.

Effect of the Particle Material

Detection efficiencies of a butanol CPC (TSI Model 3772)



Which material would be the best?

Conclusions

- The Japanese primary standard has been developed for aerosol particle number concentration.
- Calibrations at particle sizes of 10 - 200 nm, concentrations of 10^3 - 10^4 cm^{-3} , and flow rates of 1 - 1.5 L/min are possible.
- Measurement uncertainty at 95% confidence level are about 2% at 10^4 cm^{-3} and 4% at 10^3 cm^{-3} through a typical calibration procedure.
- Comparison with an OPC supported the accuracy of the standard AE.
- The selection of the particle material affects calibration results.
- The calibration service begins in October 2007.

Acknowledgements

NEDO Project “Comprehensive Technological Development of Innovative, Next-Generation, Low-Pollution Vehicles”

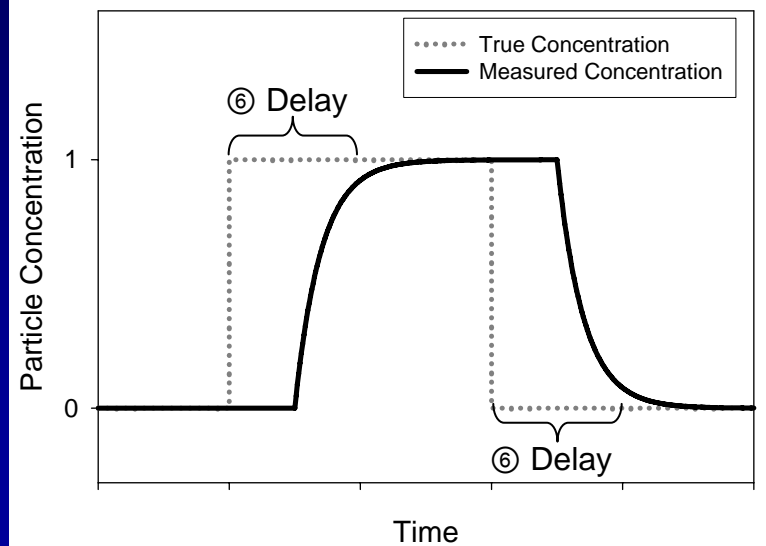
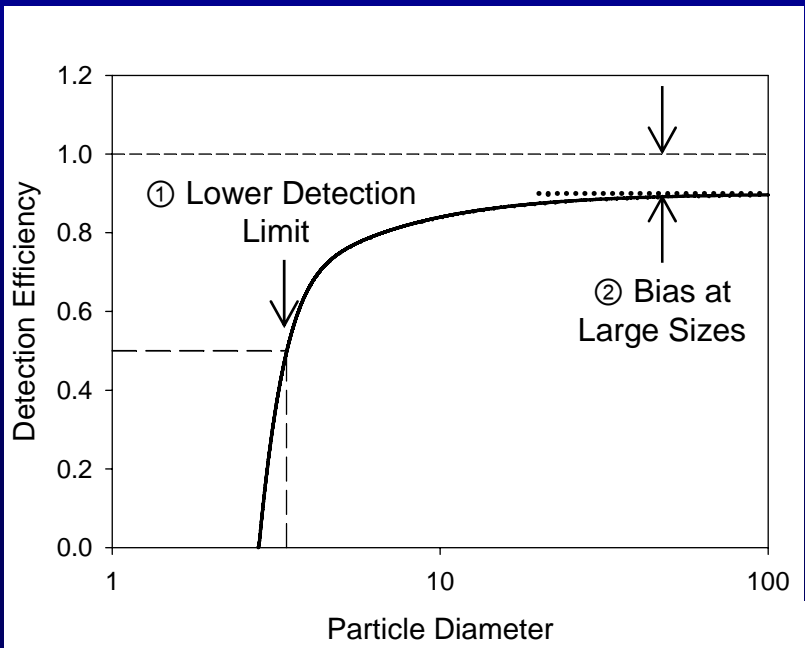
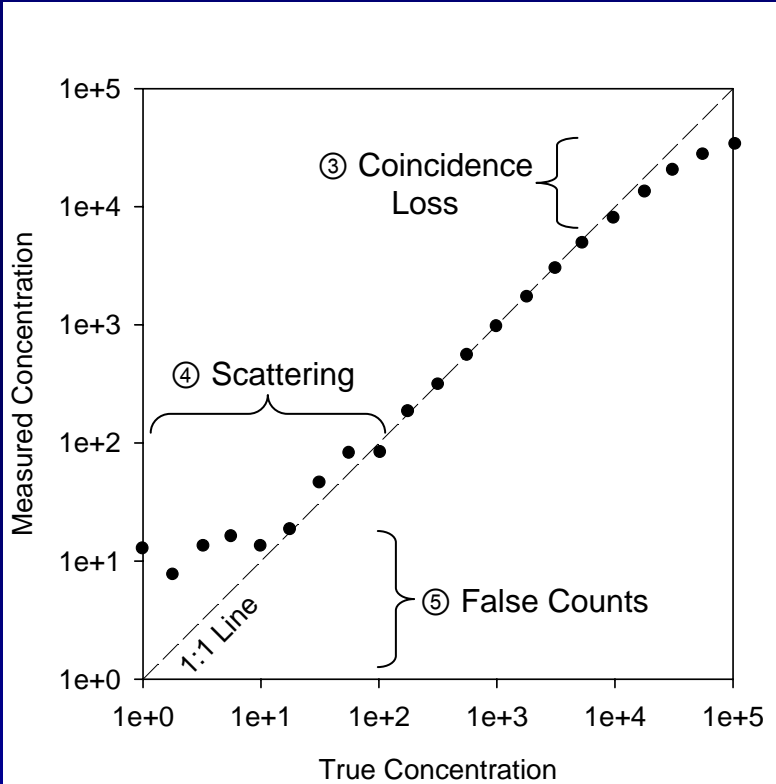
Kanomax Japan, Inc.

Rion Co. Ltd.

TSI Inc.

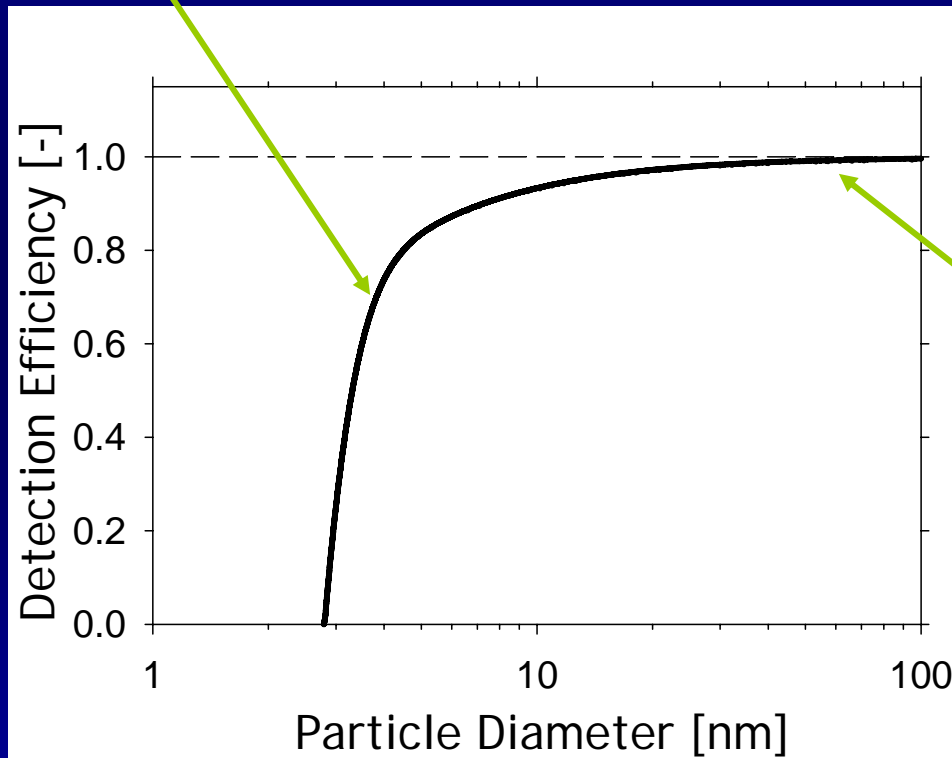
Dr. Akio Iwasa, Dr. Akira Yabe, Dr. Keizo Saito, Ms. Emiko Onuma (AIST)

CPC Characteristics



Characterization of the CPC

Where does the detection efficiency drop?



Is the detection efficiency 100% at large particle sizes?

What about the linearity of the detection efficiency against the concentration?

Uncertainty of CPC Detection Efficiency Due to Uncertainty in Particle Size

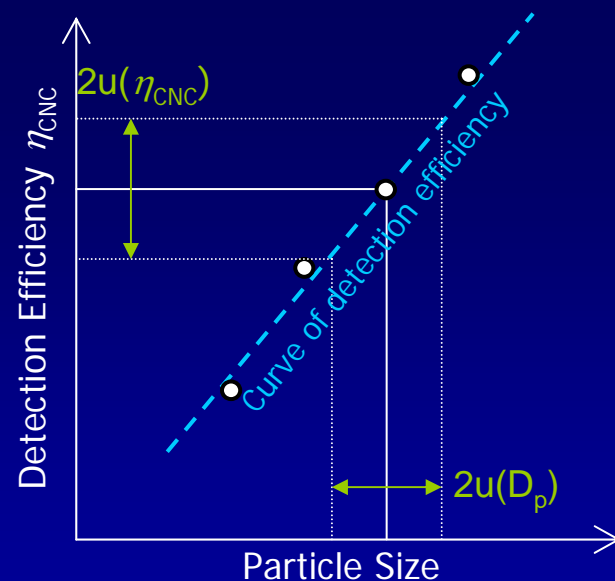
Measurement of the detection efficiency of a CNC in the size range where the efficiency varies sharply with particle size would be affected by the error in particle size. This may occur near the cut-off size of the CNC. Evaluation of the uncertainty of the size-dependent detection efficiency measurement must take this into account.

Uncertainty of the detection efficiency due to the uncertainty of particle size can be calculated as:

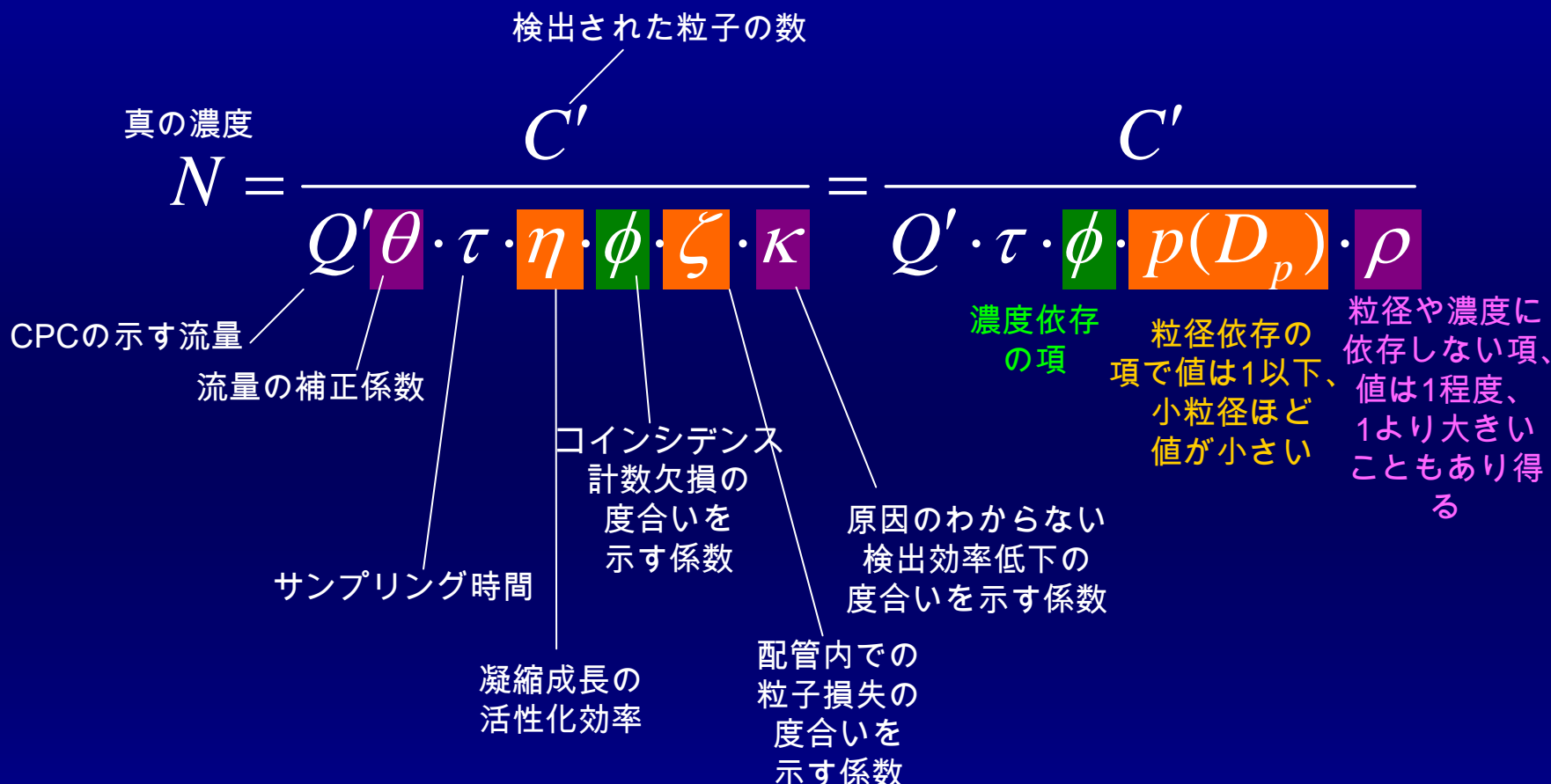
$$u(\eta_{CNC}(D_p)) = \left. \frac{d\eta_{CNC}}{dD_p} \right|_{D_p} \cdot u(D_p)$$

The slope of the detection efficiency must be obtained from the calibration result. The uncertainty of particle size would be contributed by many factors. The largest contribution would be from the uncertainty in sizing by the DMA which is calibrated with particle size standards.

Evaluation of these uncertainties is underway.



CPCによる個数濃度測定の数式モデル



- 上式は検出粒子数が多い場合に成り立つ。(粒子数が少ない場合にはポワソン統計に基づく確率分布をもつ。)
- CPCの校正では、流量を独立して校正することはない。流量の誤差は ρ に包含される。
- 校正作業では、まず、濃度が十分低く ($\phi = 1$)、かつ十分大きな粒径 ($p(D_p) = 1$) において補正係数 ρ を決定する。
- 続いて同様の濃度において粒径依存性の補正係数 $p(D_p)$ を決定する。