Development of a Primary Calibration Standard for the Aerosol Particle Number Concentration Using the Aerosol Electrometer Method

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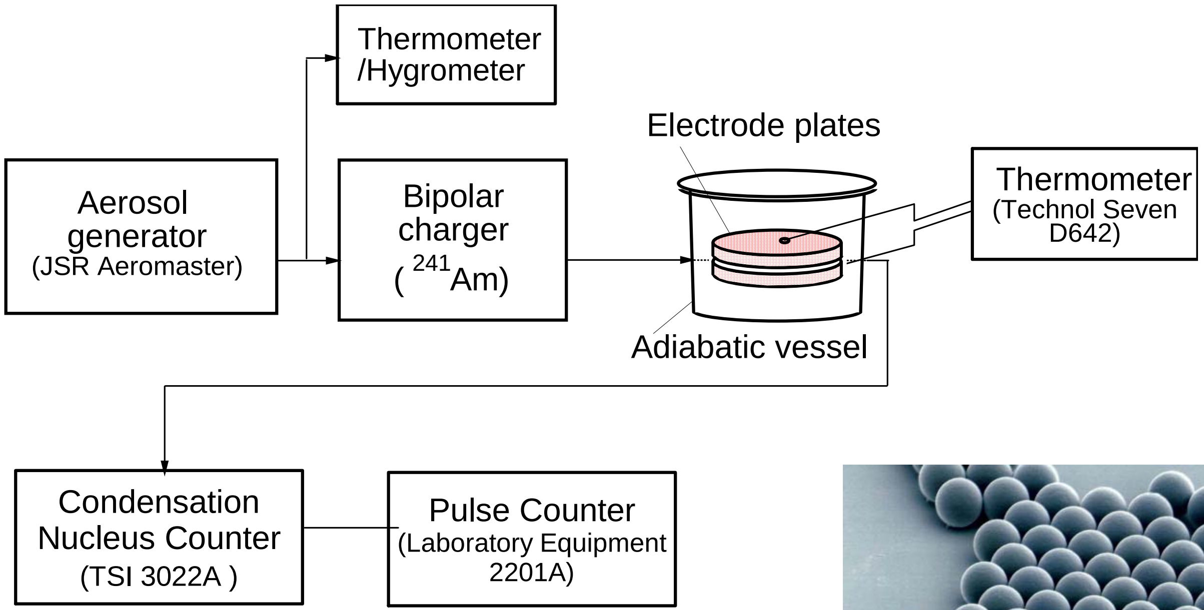
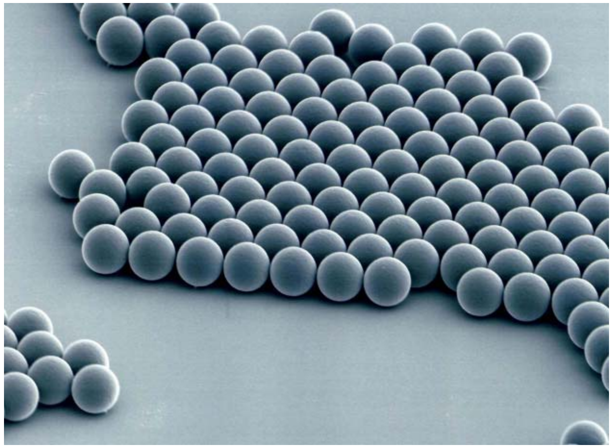
Particle Size Standard by NMIJ/AIST

Electro-gravimetric Method for Accurate Mass Determination





Outline

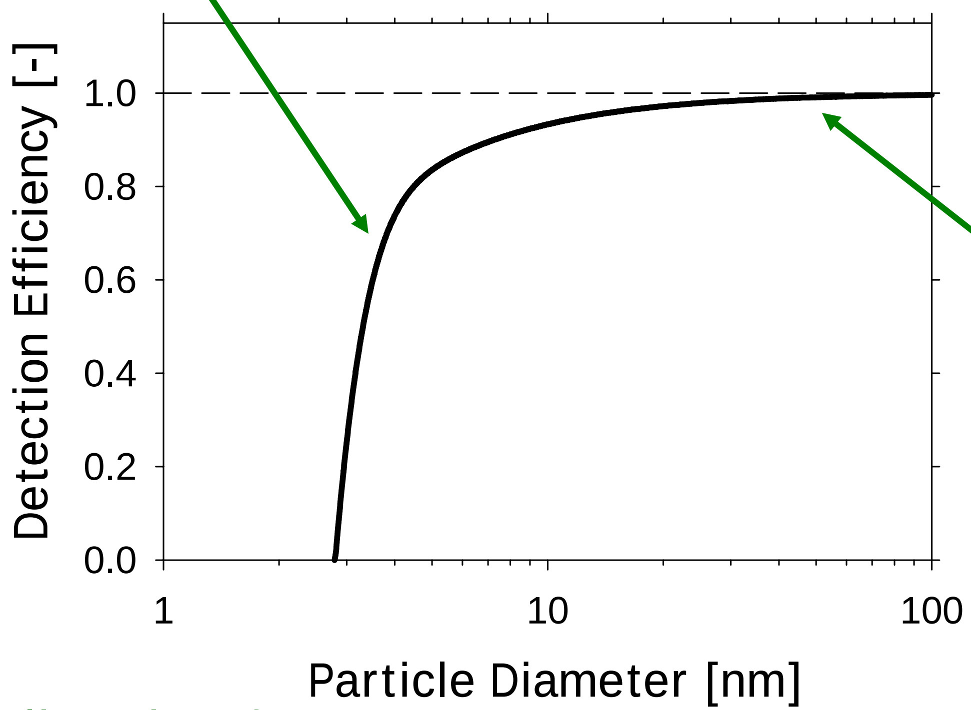
- Instruments for measuring the aerosol particle number concentration
- Current development status of the Japanese primary standard
- Estimate of the uncertainty
- Next steps

Instruments for Measuring the Aerosol Particle Number Concentration

- Light scattering
  - Optical Particle Counter (OPC)
  - Condensation Nucleus Counter (CNC)
- Electrical
  - Aerosol Electrometer (AE)

Characterization of Particle Number Concentration Measurement Instruments

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?

Development of a Primary Calibration Standard at NMIJ/AIST

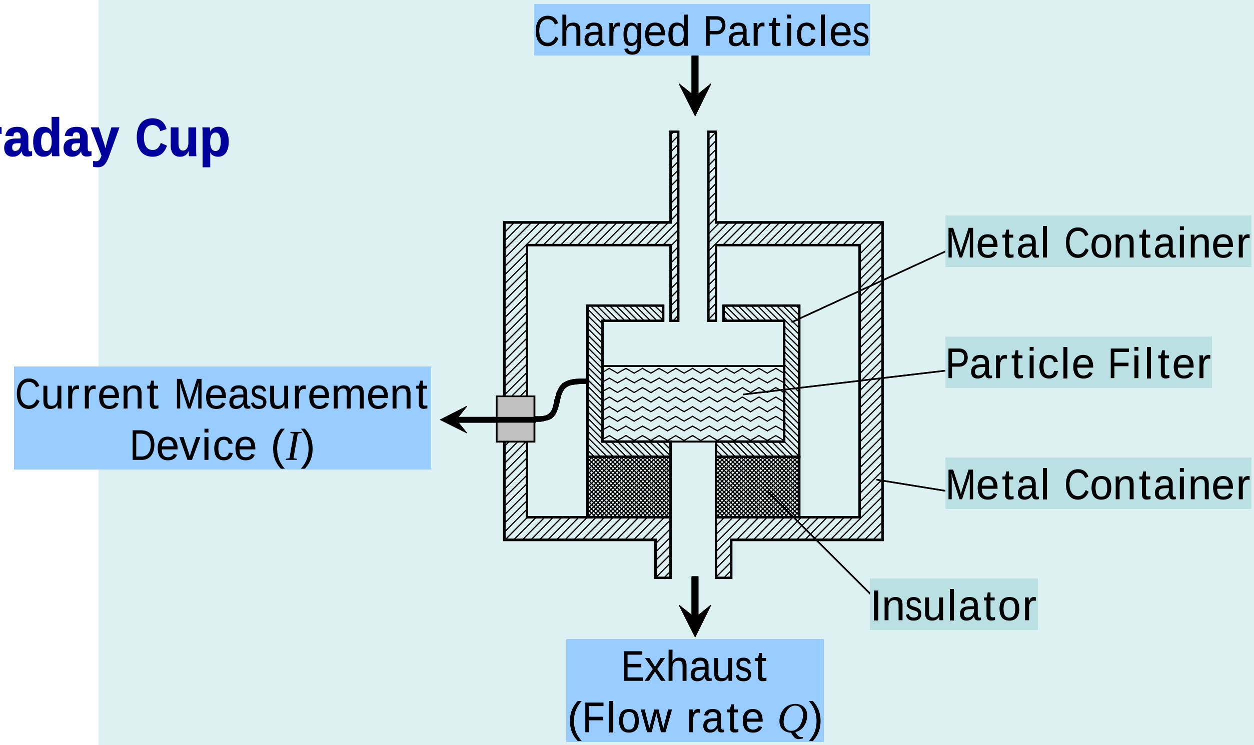
- "Primary" = the uppermost reference in the traceability chain of calibration

- Requirements for a primary standard
  - Does not need calibration with another particle number concentration standard

    (= It uses an absolute measurement method.)
  - Small measurement uncertainty
    - Accurate method
    - Well-known, well-characterized technique
    - Stable
  - Robust, durable, …
- The aerosol electrometer (AE) method was selected as an instrument for the primary standard in Japan, based on the accuracy and reliability established in previous calibration studies.

Aerosol Electrometer (AE)

Faraday Cup



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

N	Particle number concentration [cm^{-3}]
I	Current [A]
z	Average number of charges per particle [-]
e	Elementary charge (1.602 x 10^{-19} C)
Q	Volumetric flow rate [cm^3/s]
η	"Faraday cup efficiency"

Design Concepts of the Primary Standard AE

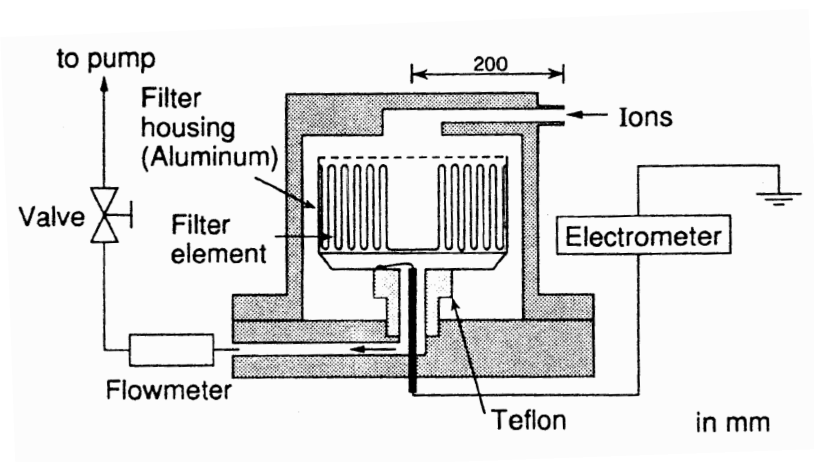
$$N = \frac{I\eta}{zeQ}$$

- Current Measurement I
  - The best instrument commercially available
  - Standard uncertainty ~3 fA; NIST-traceable
- Volumetric Flow Rate Q
  - 1 L/min
  - One of the best mass flow controller commercially available
  - Standard uncertainty 0.5%; NMIJ-traceable
- Faraday Cup
  - Designed and constructed for this standard instrument
  - High efficiency ($\eta \approx 1$) even for very small particles (e.g., below 10 nm)
    - Use high efficiency filter
    - Reduce diffusion losses of particles in the inlet tube
    - Prevent decrease of particle collection efficiency because of repulsive forces caused by charges on the filter
- Place in a controlled environment
  - constant temperature and relative humidity, low EM noise

The Inlet Design of the Primary Standard AE

Yun, Otani, and Emi, Aerosol Sci. Technol., Vol. 26, pp389-397 (1997)

TSI Original AE



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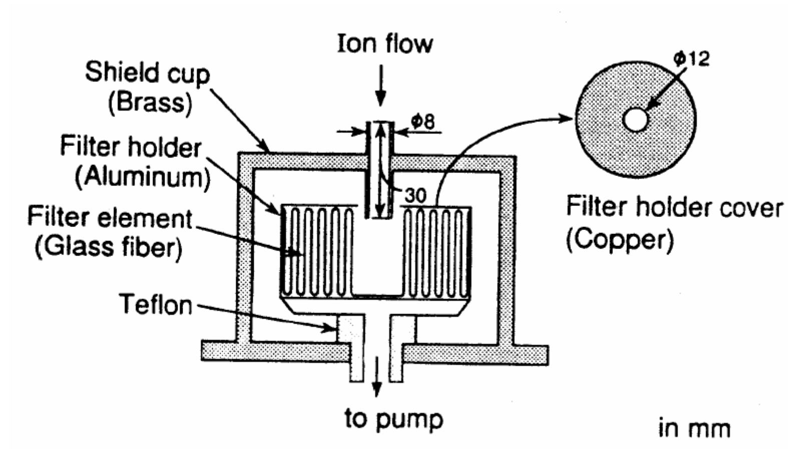


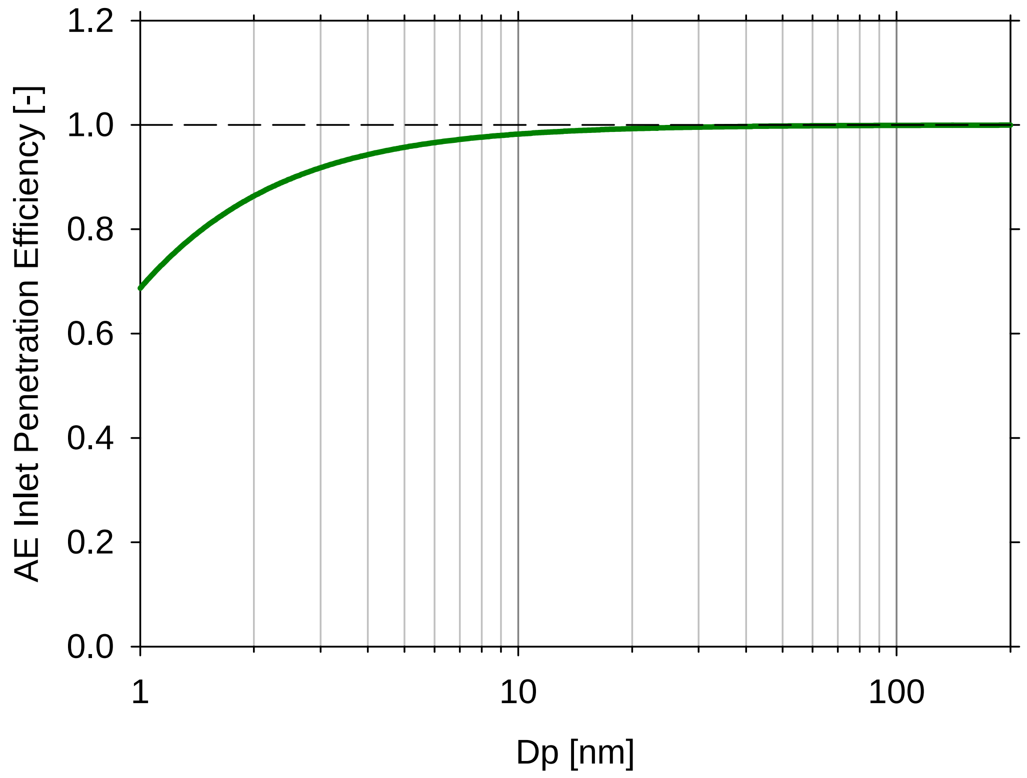
“Faraday Cup Efficiency”

- Penetration through the inlet tube

  Tube length 6 cm

  Flow Rate 1 L/min

  Gormley-Kennedy Eq.



- Filtration efficiency

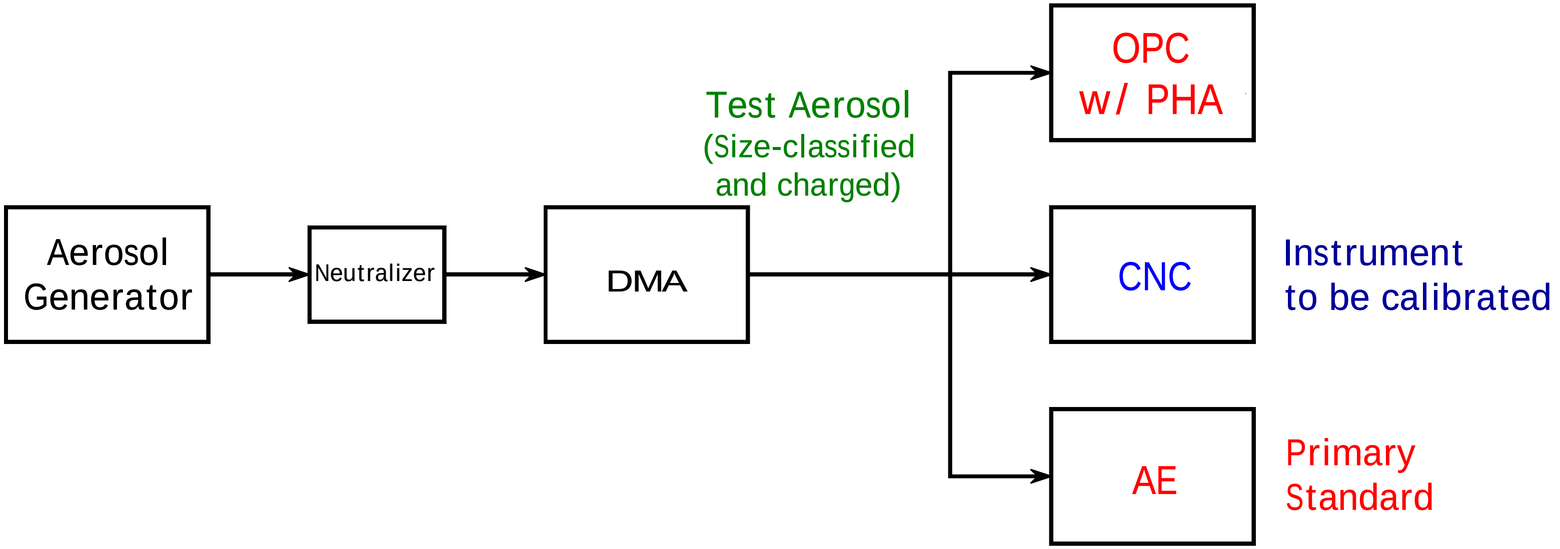
  > 99.97%

Characterization of the instrument is underway.

Calibration Setup

- Test particle supply (aerosol generator, neutralizer, DMA)
- Use electrospray for generating high-concentration aerosols

- Reduction of errors due to multiply-charged particles
  - Electrospray-generated particles are quasi-monodisperse.
  - The addition of an OPC w/ pulse height analysis tells how many multiply-charged particles are mixed.



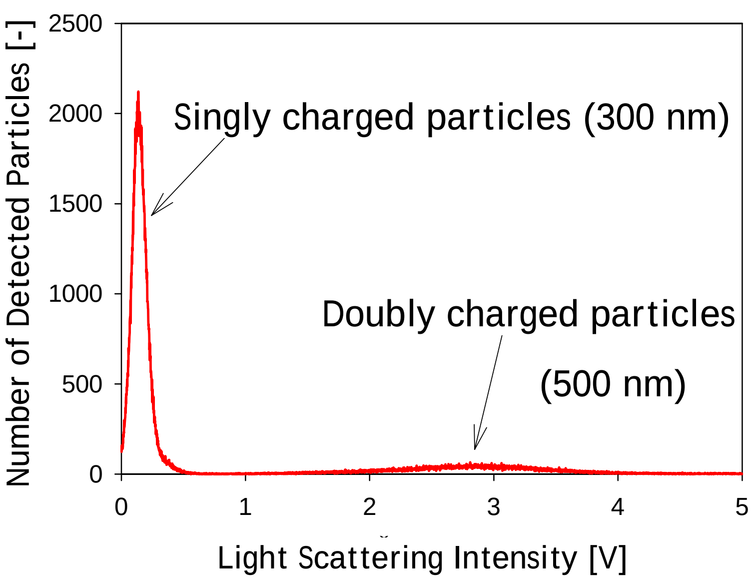
Determination of z by OPC Pulse Height Analysis

Determine the mixing ratios of particles of singly- and multiply-charged particles after DMA size-selection

Average number of charges per particles (z)

$$z = 1 \cdot f_1 + 2 \cdot f_2 + 3 \cdot f_3 + \cdots$$

$f_1, f_2, f_3, \ldots f_i$: Mixing ratios of particles of i charges



An example of the OPC pulse height analysis of DMA-selected 300-nm particles. The result gives the mixing ratios f_1 = 0.82 and f_2 = 0.18, from which z is calculated to be 1.18.

Estimate of the Uncertainty of the Primary Standard AE (including the PHA OPC)

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

N	Particle number concentration [cm^{-3}]
I	Current [A]
η	Faraday cup efficiency [-]
z	Average number of charges per particle [-]
e	Elementary charge (1.602 x 10^{-19} C)
Q	Volumetric flow rate [cm^3/s]

The law of propagation of uncertainty

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

$u_c(N)$	Combined standard uncertainty of N
$u(I)$, $u(\eta)$, $u(z)$, u(Q)	Standard uncertainty of I, η, z, and Q
$\frac{\partial N}{\partial I}, \frac{\partial N}{\partial \eta}, \frac{\partial N}{\partial z}, \frac{\partial N}{\partial Q}$	Partial derivatives (“sensitivity coefficients”)

Estimate of the Uncertainty of the Primary Standard AE (Continued)

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

$$u(I) = \frac{1}{\sqrt{3}}\left(\frac{1}{100} I + 3\ fA\right)$$ Specification of the electrometer

$$u(\eta) = \frac{1}{100}\eta$$ Estimated at 100 nm

$$u(z) = \frac{1}{100} z$$ Estimated

$$u(Q) = \frac{1}{\sqrt{3}} \cdot \frac{0.5}{100} Q$$ Specification of the mass flow controller

Example:

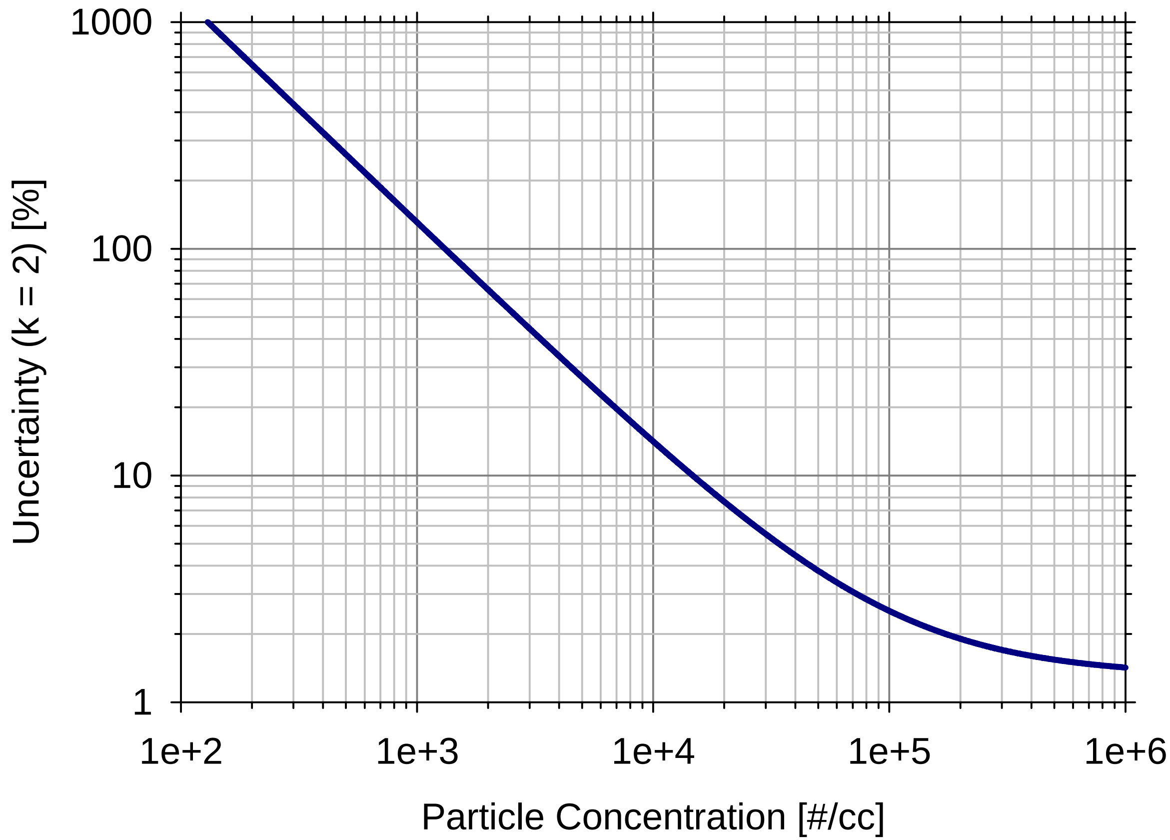
Expanded uncertainty when particle number concentration is 10^4 cm^{-3} (27 fA of current) at 1 L/min at 100 nm

$$U = 2 \cdot u_c(N) = (2)(707) = 1.4 \times 10^3\ \mathrm{cm}^{-3} \quad \text{(coverage factor } k = 2\text{; 95\% confidence level)}$$

Relative expanded uncertainty

$$U/N = 0.14$$

Concentration Dependence of the Uncertainty of the AE



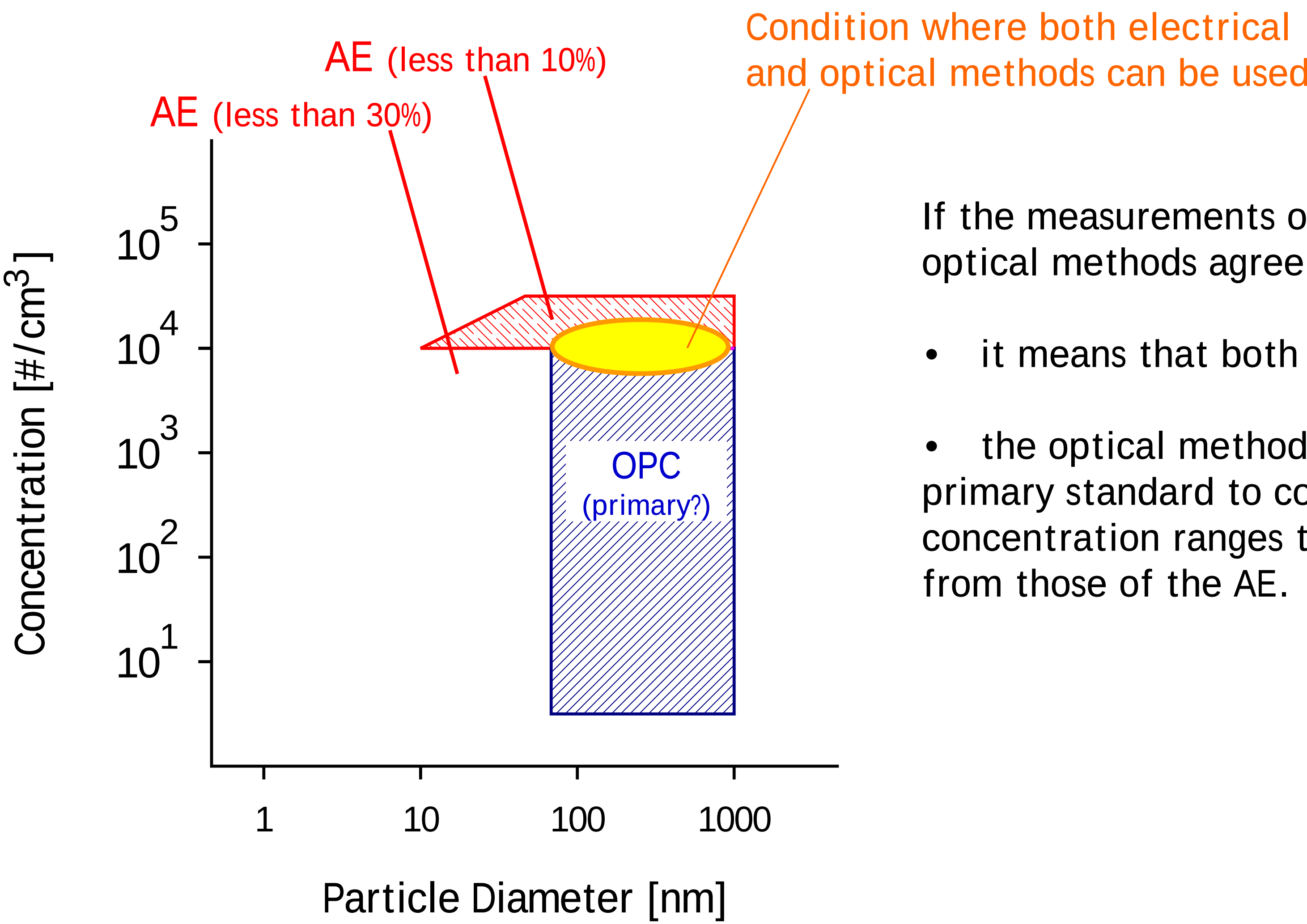
(1 L/min、100 nm, singly charged)

Next Steps for the Primary Standard AE

- Extend the size and concentration range covered by the primary standard
  - AE
    - by reduction of uncertainty in current measurement
  - Add OPC
  - Add dilution

- Comparison to standards by other countries
  - METAS (Switzerland)
  - NIST (U.S.A.)
  - others

To Cover Wider Ranges of Size and Concentration



If the measurements of the electrical and optical methods agree…,

- it means that both techniques are good;
- the optical method can be used as a primary standard to cover size and concentration ranges that are different from those of the AE.

Schedule of Calibration Services

- NMIJ-traceable calibration services are set to begin in 2007.
- Details need to be determined
  - Size
  - Concentration
  - Flow rate
  - Providers of the calibration services
  - etc.

Summary

- The aerosol particle number concentration standard is being developed in Japan based on the aerosol electrometer method, and will become available for calibration services in 2007.

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