TRACEABLE CALIBRATION OF CONDENSATION PARTICLE COUNTERS WITH RESPECT TO SMALLEST PARTICLE SIZE DETECTION LIMIT, COUNTING EFFICIENCY, AND CONCENTRATION LINEARITY

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Abstract

For nearly 25 years, TSI condensation particle counters (CPCs) have been extensively used by researchers, including automobile and truck manufacturers, to measure the number concentration and, as part of a scanning mobility particle sizer (SMPS™) system, the size distribution of particle emissions from diesel and spark ignition engines. As proposed by the GRPE Particle Measurement Programme (PMP), a CPC shall be used to measure the particle number concentration of exhaust emissions during drive cycles for regulatory compliance or vehicle type-approval purposes. Therefore, it is essential to calibrate CPCs using a traceable and independent method to ensure proper measurement performance. This study illustrates a traceable method of calibrating the smallest particle size detection limit, particle counting efficiency, and particle concentration linearity of CPCs by simultaneously testing several TSI Model 3010 CPCs (Caldow et al. 1992) using a commercially available aerosol electrometer as the traceable reference. In addition, it demonstrates the effects of a modification of CPC operating parameters to increase its lower particle size detection limit from approximately 10nm to greater than 20nm to meet PMP's desire to prevent measurement of volatile and semi-volatile nanoparticles formed by nucleation of gaseous compounds.

Introduction

One of the main concerns and opposing arguments against the use of a CPC to measure particle number concentration for regulatory compliance testing is the objection that there is no method to calibrate CPCs. Certainly, this objection is not correct as "primary" methods for CPC calibration have been described extensively in literature and applied for many years (Nolan and Pollak 1946, Pollak and Metnieks 1959, Liu and Pui 1974, Agarwal and Sem 1978, Pui and Liu 1979). In general, the calibration of a CPC requires producing a quasi-stable, monodisperse aerosol, simultaneously delivering it into both the CPC under calibration and a sensitive aerosol electrometer for measurement, and comparing the number concentration readings of the CPC against the electrometer reading. The aerosol electrometer is used as the primary reference detector. To calibrate a CPC's smallest particle size detection limit and counting efficiency, this procedure is repeated for several particle sizes to produce a CPC counting efficiency curve (0 to 100%). To measure a CPC's response linearity, the same procedure is repeated at several aerosol concentrations for a particle size that is large enough so that the CPC's counting efficiency is about 100%.

Calibration Method

In this study, a modified method is shown that employs a stable, high-concentration electrospray aerosol generator (EAG) as the primary aerosol source (Chen et al. 1995). Emery oil particles were generated using the EAG and subsequently size-selected with an electrostatic classifier. The classifier uses a differential mobility analyzer (DMA) to select particles within a narrow range of electrical mobility, which are essentially monodisperse particles in the size range of interest for CPC calibration. Emery oil was chosen because it consists of ~82% of C30 and ~16% of C40 polyolefin by volume and is representative of compounds used in engine lubricating oil. The electrospray aerosol generator produces a polydisperse aerosol with a sharp peak at the particle size of interest. The peak size was then selected using the DMA to produce a highly monodisperse aerosol. A SMPS configured with a nano-DMA and an ultrafine CPC (UCPC) was used to prove the monodispersity of this aerosol by measuring its size spectrum. The SMPS measurements of 22nm particles showed a geometric standard deviation (GSD) of 1.46 for particles exiting the electrospray and 1.04 after the DMA classification. No other peaks were observed in the SMPS data, which indicates the absence of multiply-charged particles that would influence the concentration readings calculated based on the aerosol electrometer measurement. Tests repeated for EAG-generated, DMA-classified 50nm and 90nm particles exhibited GSD values of 1.04 and 1.11, respectively, which verified the monodispersity of our calibration aerosol. Only a negligible (< 1%) amount of doubly-charged particles was observed in the SMPS data for 90 nm particles.

The monodisperse aerosol exiting the DMA was mixed uniformly with particle-free, HEPA-filtered air and was split equally into the aerosol electrometer and several CPCs. The aerosol electrometer operates on the principle of the Faraday cup. It consists of a current sensor which measures the total electrical current of the monodisperse particles collected on an absolute filter. It converts the current signal into a voltage across a precision (1% accuracy) resistor with a known resistance. The current (amperes) measured by the electrometer is related to the input aerosol concentration N (particles/cm^3) by equation:

$$I = N\, n_p\, e\, q_e\,,$$

where n_p (number of elementary charge units) is the charge on a single particle, e (= 1.6×10^{-19} coulomb) is the elementary unit of charge, and q_e (cm^3/s) is the volumetric flow rate of the aerosol entering the electrometer. When the particle charge is known, the particle number concentration can be accurately calculated using this equation. Because the SMPS data exhibited only a single monodisperse peak with no noticeable influence of multiple-charged particles, a single charge (n_p = 1) is valid for the reference concentration calculation.

Comparing the coincidence-corrected number concentration readings of the CPC against the concentrations calculated using the electrometer reading, the counting efficiency of the CPC is obtained for the selected particle size.

Calibration of Smallest Particle Size Detection Limit and Counting Efficiency

Challenge aerosol generated as described above was used to calibrate the counting efficiencies of five standard Model 3010 CPCs against the aerosol electrometer. Fourteen particle sizes in the range of 4.5 to 95nm were produced. This range includes the smallest particle size detection limit of the 3010 CPCs. The counting efficiency curves of the CPCs were generated using curve fit software. Unit to unit comparison results matched very well. The D_{10}, D_{25}, D_{50}, D_{75} and D_{90} values (i.e. particle sizes at 10, 25, 50, 75, and 90% counting efficiencies) for these five CPCs were in the range of 6.8 ± 0.4nm, 7.9 ± 0.5nm, 9.4 ± 0.5nm, 11.4 ± 0.4nm, and 13.5 ± 0.5nm, respectively.

Concentration Linearity

The concentration linearity response of four standard Model 3010 CPCs was tested with monodisperse 50nm emery oil particles and again compared against the aerosol electrometer. Particles of 50 nm in diameter were used as the CPC counting efficiency at that size should be close to 100%. Six particle concentration levels that were approximately equally spaced ranging from 0 to about 10,000 particles/cm^3 (0, 2000, 4000, 6000, 8000, and 10,000 particles/cm^3) were generated using a dilution bridge. The response of the CPCs was seen to be linear up to the maximum concentration tested. Moreover, the tests demonstrated a near-flawless linear measurement response for each of the CPCs. Concentration linearity slopes ranged from 0.953 to 0.973, with correlation coefficients (R^2) greater than 0.998 for all four CPCs.

<u>Traceability of the Calibration Method</u>

The traceability of the above-described calibration method depends on the traceability of the DMA for generating singly-charged, monodisperse particles of a known size and the aerosol electrometer as the particle number concentration reference detector.

The operating principle of the electrostatic classifier and the DMA is based on electrical mobility. For a cylindrical DMA, electrical mobility of particles selected is a function of the flow rates (the polydisperse/monodisperse aerosol flow rate ($q_p = q_m$ for the DMA) and the total flow rate ($q_t = q_p + q_s$ where q_s is the sheath air flow rate)), geometric parameters of the DMA (the inner radius of the outer electrode (r_2), the outer radius of the inner electrode (r_1), and the characteristic length between the aerosol inlet and outlet slits (L)), and the voltage (V) on the center electrode (Kinney et al. 1991). The sheath air flow rate is measured with a built-in NIST traceable flow meter. The aerosol flow rate inside the DMA equals the flow rate coming out of the EAG, which can be easily measured with a NIST traceable flow meter. With regard to the geometric parameters of the DMA, such components are precisely machined and can be measured with NIST traceable bore gage, micrometer and caliper. In addition, the high voltage of the DMA is calibrated with an NIST traceable kilovolt divider.

As stated earlier, the aerosol electrometer operates on the Faraday cup principle. The particle number concentration is calculated based on the particle charge (n_p), the sample flow rate (q_e), and the resistance of the embedded resistor (R) that converts current into voltage. The calibration particles have been verified to be singly-charged in the size range of interest with the SMPS measurements. The sample flow rate is measured with a built-in NIST traceable flow meter. The embedded resistor was measured by the manufacturer with a NIST traceable standard to ensure its resistance was within ±1% of the nominal value. The current measurement accuracy of the electrometer is further calibrated with several known currents generated by a NIST traceable DC voltage divider and a resistor assembly which is calibrated periodically against a NIST traceable standard by a local calibration test house.

<u>CPC Parameter Modifications to Increase the Lower Particle Size Detection Limit</u>

The PMP specifies that semi-volatile and volatile particles that are formed by nucleation of gaseous components as the exhaust cools shall not be measured. While the primary method of eliminating such volatile particles from the measurement is a pretreatment step referred to as “thermodilution,” the measurement system will enjoy a secondary safety factor if the smallest particle size detection limit of the CPC can be adjusted to 20nm, or larger. This study also investigated whether or not the smallest detection limit of the CPC could be adjusted to a larger size by changing the internal operating parameters of the Model 3010 CPC in a controlled manner.

We modified the condenser and saturator temperature settings of five Model 3010 CPCs to effectively make them less sensitive to smaller particle sizes, i.e. the range of nucleation mode particles. Using the same calibration test setup and method described above, the smallest particle size detection limit, counting efficiency, and response linearity of each modified CPC were evaluated. The results show that the 50% detection limit (D_{50}) of the 3010 CPC can be adjusted from 10nm to larger than 20nm with no adverse effect on the sharpness of the detection curve. A D_{50} value in the range of 21.7 ± 0.4nm was found for the five modified 3010 CPCs under test. In addition, the particle detection efficiency curve is much steeper than can be obtained by using one or more diffusion screens upstream of the CPC inlet. Therefore, compared to standard 3010

CPCs fitted with diffusion screens, the modified CPCs offer a more reliable and accurate concentration measurement in the presence of nucleation mode particles. We also performed concentration linearity tests on three of the modified CPCs. The results show the concentration linearity slopes ranged from 0.966 to 0.969, with correlation coefficients (R^2) greater than 0.998 for all three of the modified 3010 CPCs. The modified CPC, now introduced as the Model 3010D CPC, fulfills the lower size detection characteristics proposed by the PMP for particle number concentration measurements.

Conclusions

A method for calibrating CPCs has been described. The combination of an electrospray aerosol generator, electrostatic classifier with DMA, and an aerosol electrometer has been shown to offer an independent method for calibrating CPCs. This calibration system is fully capable of calibrating CPCs' smallest particle size detection limit, particle counting efficiency curve, and concentration linearity, which are critical for CPCs used for emission testing during drive cycles for regulatory compliance or vehicle type-approval purposes. The 50% particle size detection limit of standard TSI 3010 CPCs are in the range of 9 to 10 nm. Concentration linearity test results show a slope between 0.953 to 0.973 with $R^2 > 0.998$. The calibration apparatus, in particular, the electrostatic classifier with DMA and aerosol electrometer is capable of offering NIST traceability for calibrating CPCs.

In addition, it has been shown possible to modify the internal operating parameters of the Model 3010 CPC, effectively increasing the 50% particle size detection limit of 3010 CPCs from 10nm to larger than 20nm. The Model 3010D CPCs will provide a secondary safety factor to the primary method of thermodilution, to exclude the measurements of semi-volatile and volatile particles that are formed by nucleation of gaseous components as the exhaust cools. The response of these 3010D CPCs is also linear with a slope of about 0.97 and $R^2 > 0.998$. In addition, the 3010D CPCs have a much sharper efficiency curve than the standard 3010 CPCs with one or more layers of diffusion screens upstream of the CPCs.

References

Agarwal J.K., and G.J. Sem [1978] "Generating Submicron Monodisperse Aerosols for Instrument Calibrations," TSI Quarterly, May/June, p 5, TSI Incorporated, St. Paul, MN, USA.

Caldow R., M.R. Palmer, and F.R. Quant [1992] "Performance of the TSI Model 3010 Condensation Particle Counter," Proc. AAAR Annual Meeting, October 12-16, 1992, San Francisco, CA, USA.

Chen, D.-R., D.Y.H. Pui, and S.L. Kaufman [1995] "Electrospraying of Conducting Liquids for Monodisperse Aerosol Generation in the 4 nm to 1.8 µm Diameter Range," J. Aerosol Sci., 26(6):963-977.

Kinney, P.D., D.Y.H. Pui, G.W. Mulholland, and N.P. Bryner [1991] "Use of the Electrostatic Classification Method to Size 0.1 µm SRM Particles - A Feasibility Study," Journal of Research of the National Institute of Standards and Technology, 96(2):147-176.

Liu B.Y.H., and D.Y.H. Pui [1974] "A Submicron Aerosol Standard and the Primary, Absolute Calibration of the Condensation Nuclei Counter," J. Colloid Interface Sci. 47(1):155–171.

Nolan, P.J., and L.W. Pollak [1946] "The Calibration of a Photoelectric Nucleus Counter," Proc. Royal Irish Acad., A9:9–31.

Pollak, L.W., and A.L. Metnieks [1959] "New Calibration of Photoelectric Nucleus Counters," Geofis. Pura Appl., 43:285–301.

Pui, D.Y.H., and B.Y.H. Liu [1979] "Aerosol Generation and Calibration of Instruments," TSI Quarterly, May/June, V(2):5-12, TSI Incorporated, St. Paul, MN, USA

Traceable Calibration of Condensation Particle Counters
with Respect to
Smallest Particle Size Detection Limit, Counting Efficiency, and Concentration Linearity

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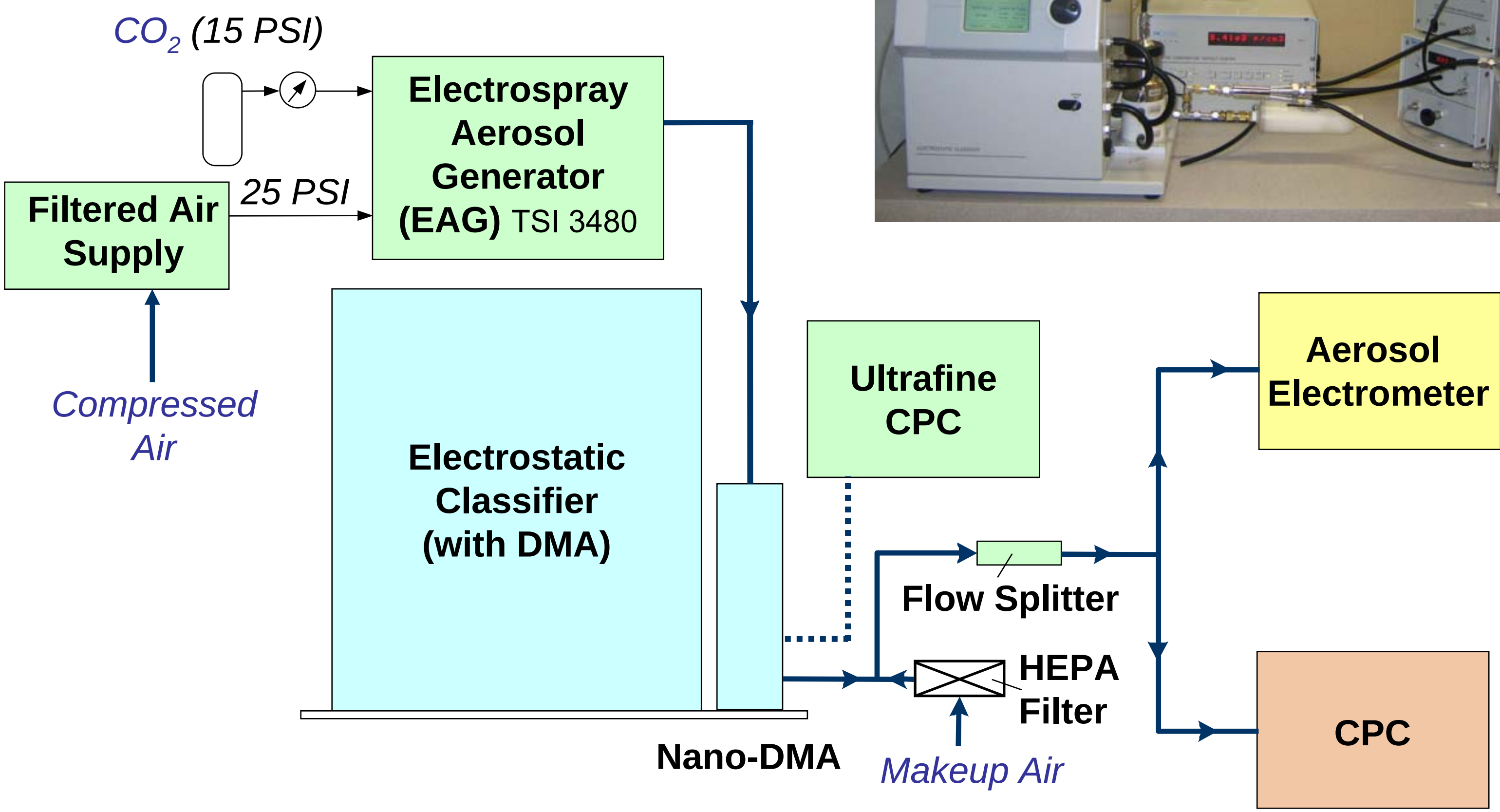
Outline

- Introduction: Why traceable calibration ?
- Calibration setup and method
- Experimental details
- Test results: counting efficiency & linearity for standard TSI Model 3010 CPC
- Traceability of calibration method
- Modifications for PMP and test results for the new Model 3010D CPC
- Conclusions

Why Traceable Calibration?

- Condensation particle counters (CPCs) have been used to measure number concentration of ultrafine particles for ~25 years
  - As part of scanning mobility particle sizer (SMPS™) to measure size distributions as well
- GRPE Particle Measurement Programme (PMP) proposed CPC for measurement of particle number concentration for <u>regulatory</u> compliance
  - Hence, calibration of CPCs using traceable method to ensure proper performance is required
- Method to calibrate smallest particle size detection limit, counting efficiency, & concentration linearity of CPCs is demonstrated

Calibration Setup and Method



- EAG generates emery oil particles
- DMA selects singly-charged, monodisperse particles of known size
- Monodisperse aerosol mixes uniformly with filtered air & splits equally into aerosol electrometer and CPCs under test
- CPC counting efficiency = ratio of CPC and electrometer readings

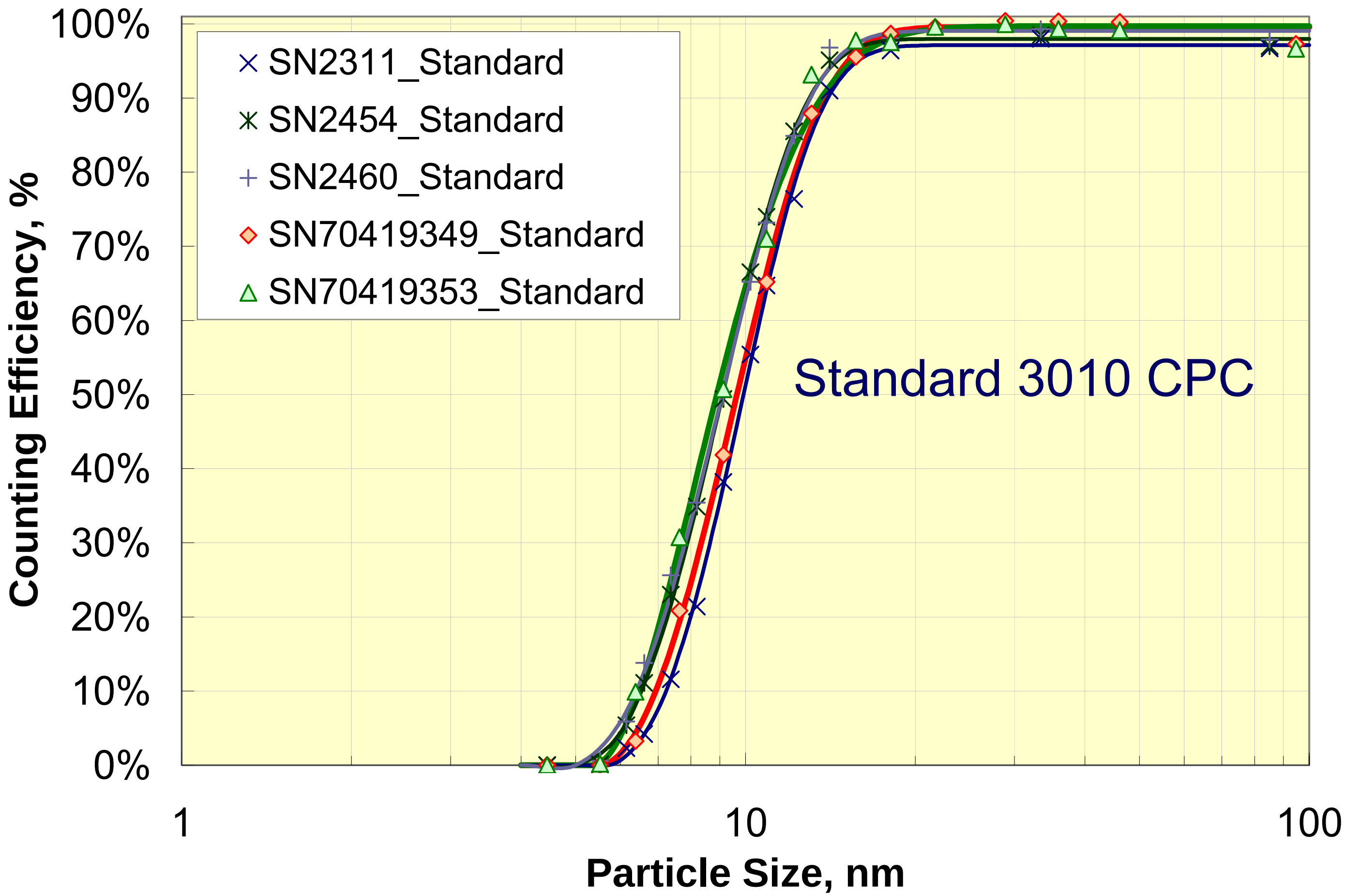
Smallest Particle Size & Counting Efficiency

- 10 – 14 particle sizes (4.5 – 95 nm) used to create counting efficiency curve
- Particle concentration < 10^4 P/cm^3
- CPCs tested simultaneously
- To eliminate need for diffusion loss correction
  - Equal tube lengths from flow splitter to electrometer and CPCs
  - Equal flow rates for electrometer and CPCs
- CPC concentrations corrected for coincidence

Linearity Test

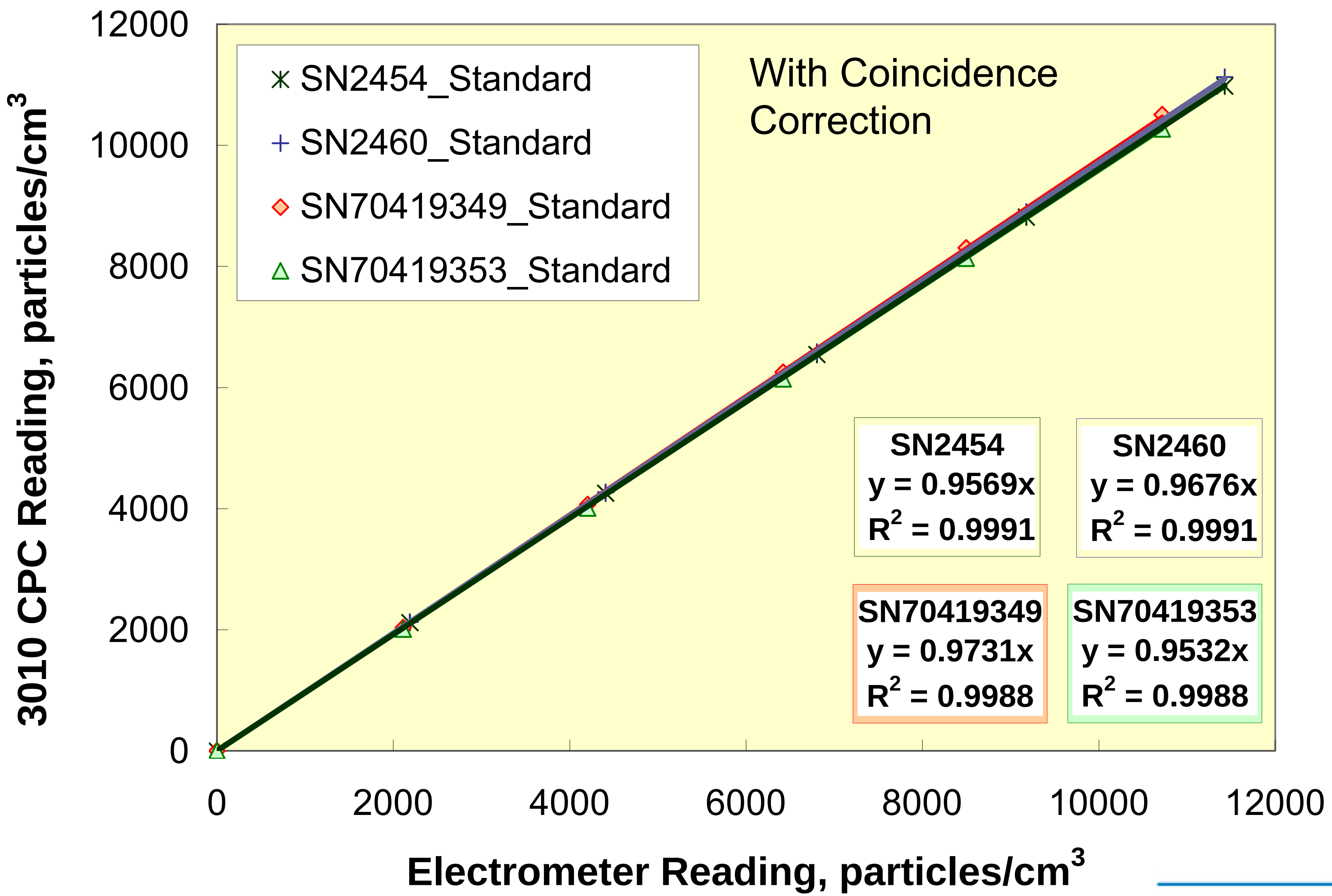
- 50 nm particles chosen for ~100% counting efficiency for CPC
- Six concentrations levels
  - Approximately equally spaced from 0 - 10^4 P/cm^3

Results: Counting Efficiency of 3010



	SN2311_S	SN2454_S	SN2460_S	SN70419349_S	SN70419353_S	Size Range
D10, nm	7.2	6.5	6.4	6.9	6.5	6.8 ± 0.4
D25, nm	8.3	7.6	7.5	8.0	7.4	7.9 ± 0.5
D50, nm	9.9	9.1	9.1	9.7	8.9	9.4 ± 0.5
D75, nm	11.9	11.0	11.0	11.7	11.1	11.4 ± 0.4
D90, nm	14.0	13.0	13.0	13.8	13.6	13.5 ± 0.5

Results: Linearity Response of 3010



Slope = 0.953 to 0.973

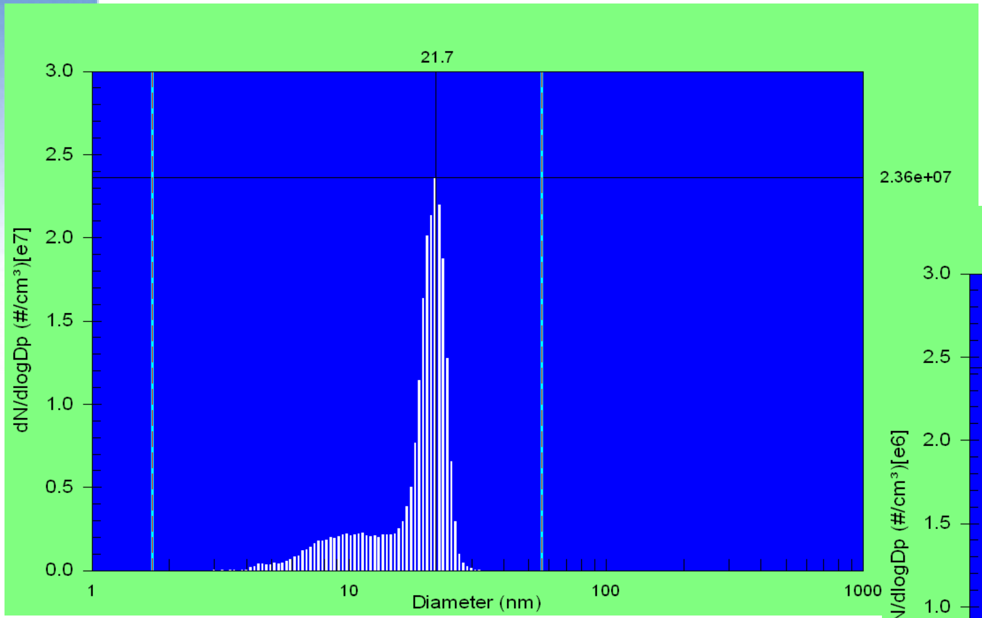
R^2 > 0.998

Traceability of the CPC calibration method depends on:

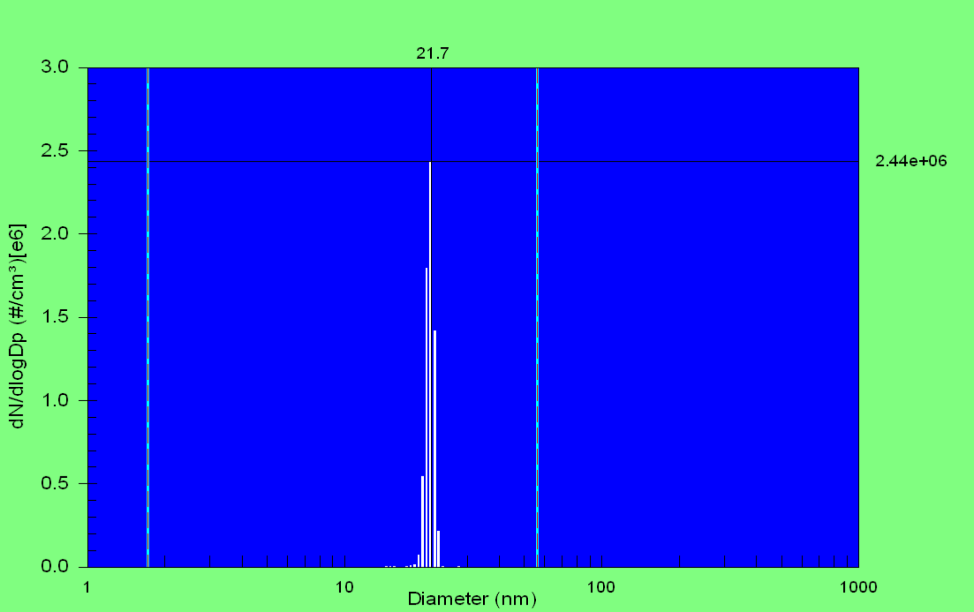
- The ability of generating singly-charged, monodisperse particles of known size
- The ability of measuring particle concentration accurately using a reference aerosol detector

Monodispersity of Particles

Step 1: Particles Generated by Electrospray (22 nm, GSD = 1.46)



Step 2: Particles Generated by Electrospray and Selected by DMA (22 nm, GSD = 1.04)



Electrospray-generated, DMA-selected Particles:

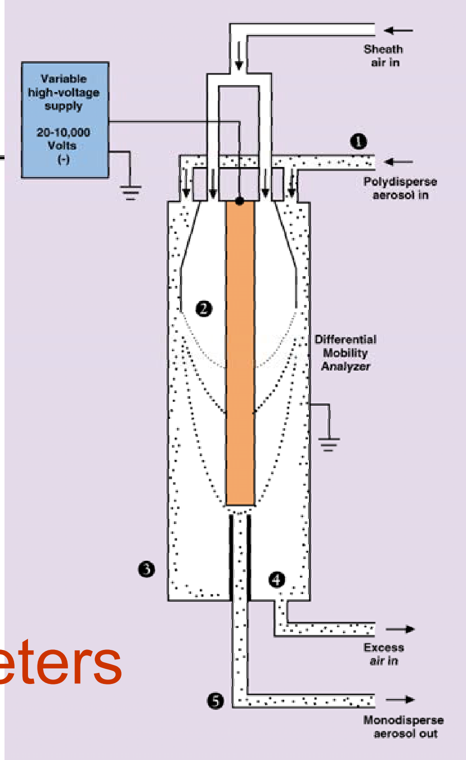
50 nm: GSD = 1.04

90 nm: GSD = 1.11

Traceability – DMA

In a cylindrical DMA, Z_p of selected particles is

$$Z_p = \frac{[q_t - 1/2(q_p + q_m)]\ln(r_2/r_1)}{2\pi VL}$$



- Flow rates (q_t=q_s+q_p) – NIST traceable flow meters
  - Sheath flow rate (q_s)
  - Polydisperse/Monodisperse aerosol flow rate (q_p = q_m)
- Geometric parameters – NIST traceable bore gage, micrometer, and caliper
  - r_1 / r_2 = inner / outer electrode radius
  - L = characteristic length between aerosol inlet/outlet slits
- Voltage on center electrode (V) – calibrated with NIST traceable kilovolt divider

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Traceability – Aerosol Electrometer

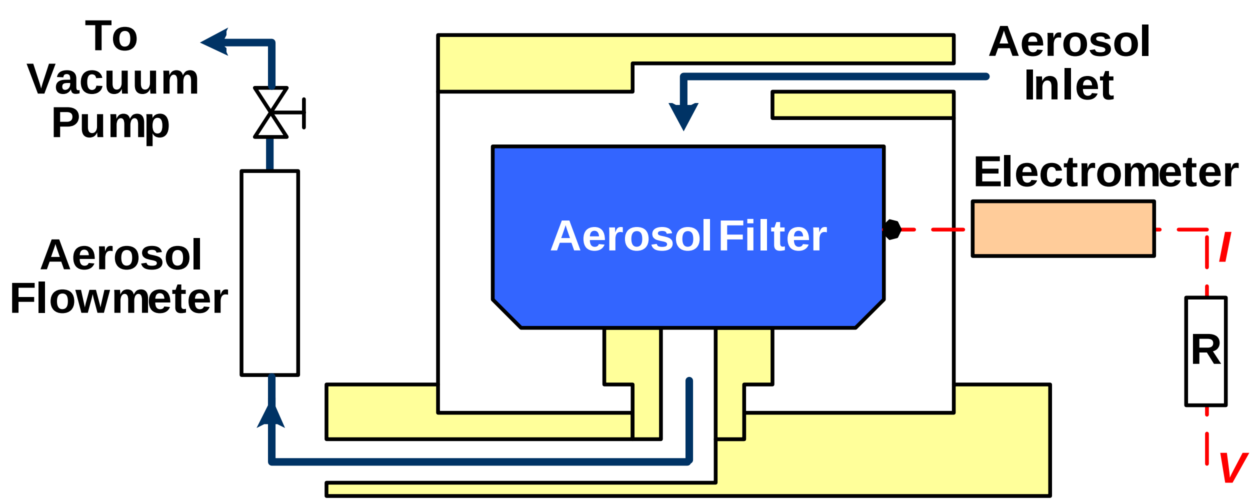
$$N = \frac{V}{e \cdot R \cdot n_p \cdot q_e}$$

where:

N = particle number concentration

V = electrometer voltage reading (IR)

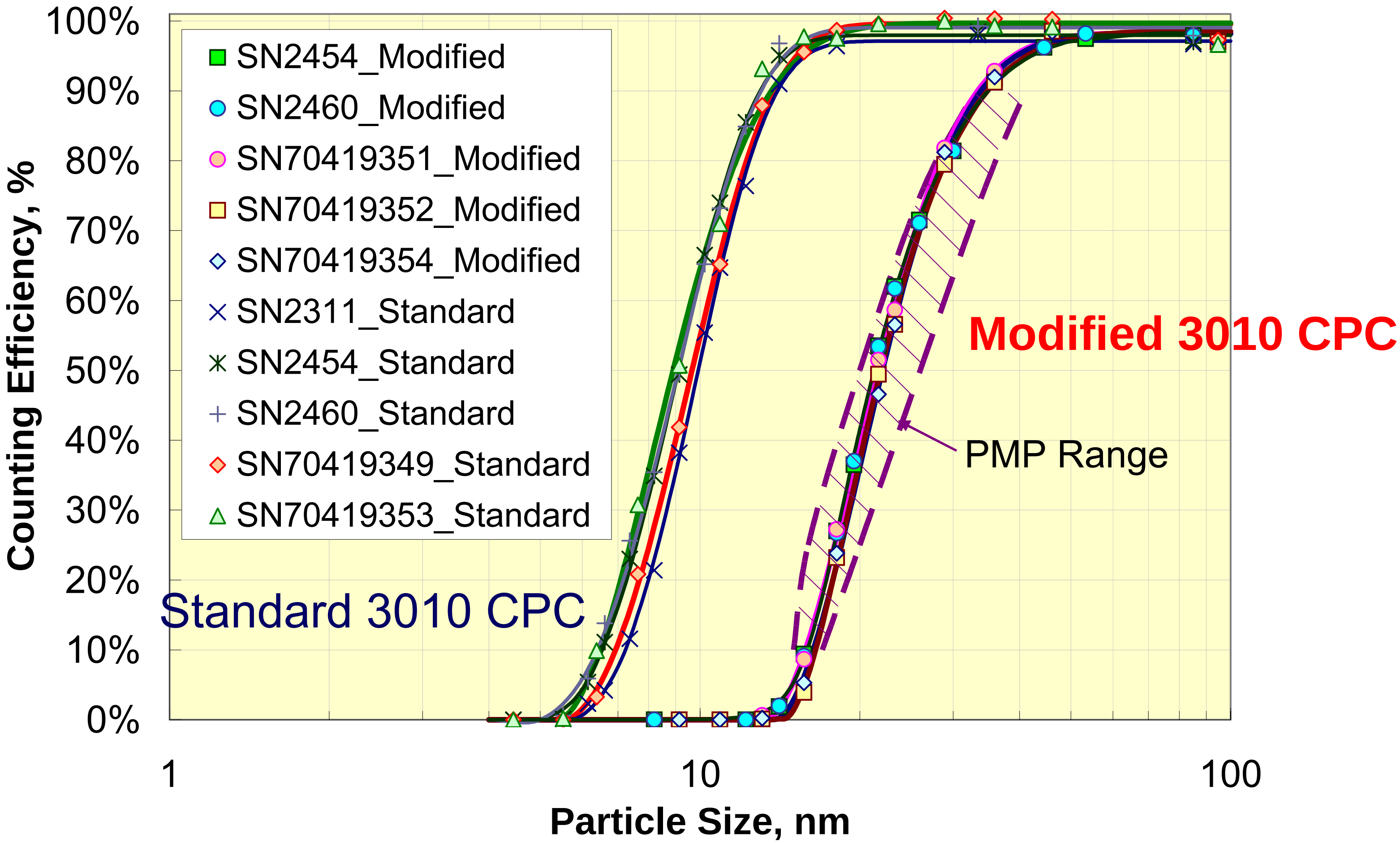
- Unit charge (e) – constant (1.602×10^{-19} C)
- Resistor (R) – 1% precision, measured by manufacturer using NIST traceable standard
- Particle charge (n_p) – verified to be unity (1.0) by SMPS
- Flow rate (q_e) – NIST traceable flow meter



Modifications for PMP

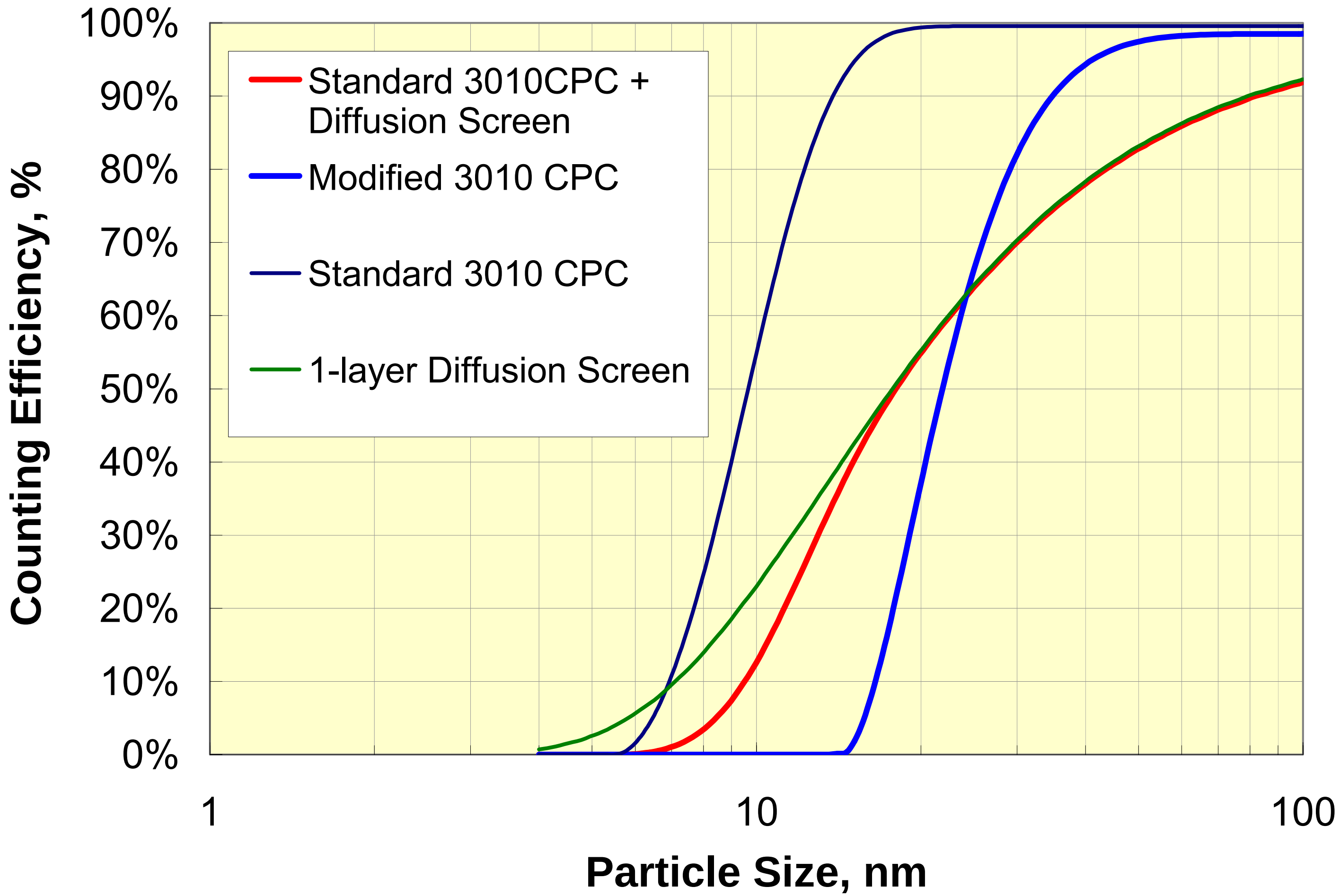
- PMP specifies that volatile nanoparticles formed by nucleation of gaseous components shall be eliminated from measurement
  - Primary method of removing volatile particles is "thermodilution"
  - Secondary safety factor if **smallest particle size detection limit of CPC** can be adjusted to ≥ 20nm
  - PMP has considered diffusion screens
- Adjusted the lower detection limit of 3010 CPCs by changing internal operating parameters in a controlled manner
- Counting efficiency and linearity of several modified 3010 CPCs were tested

PMP CPC – Counting Efficiency



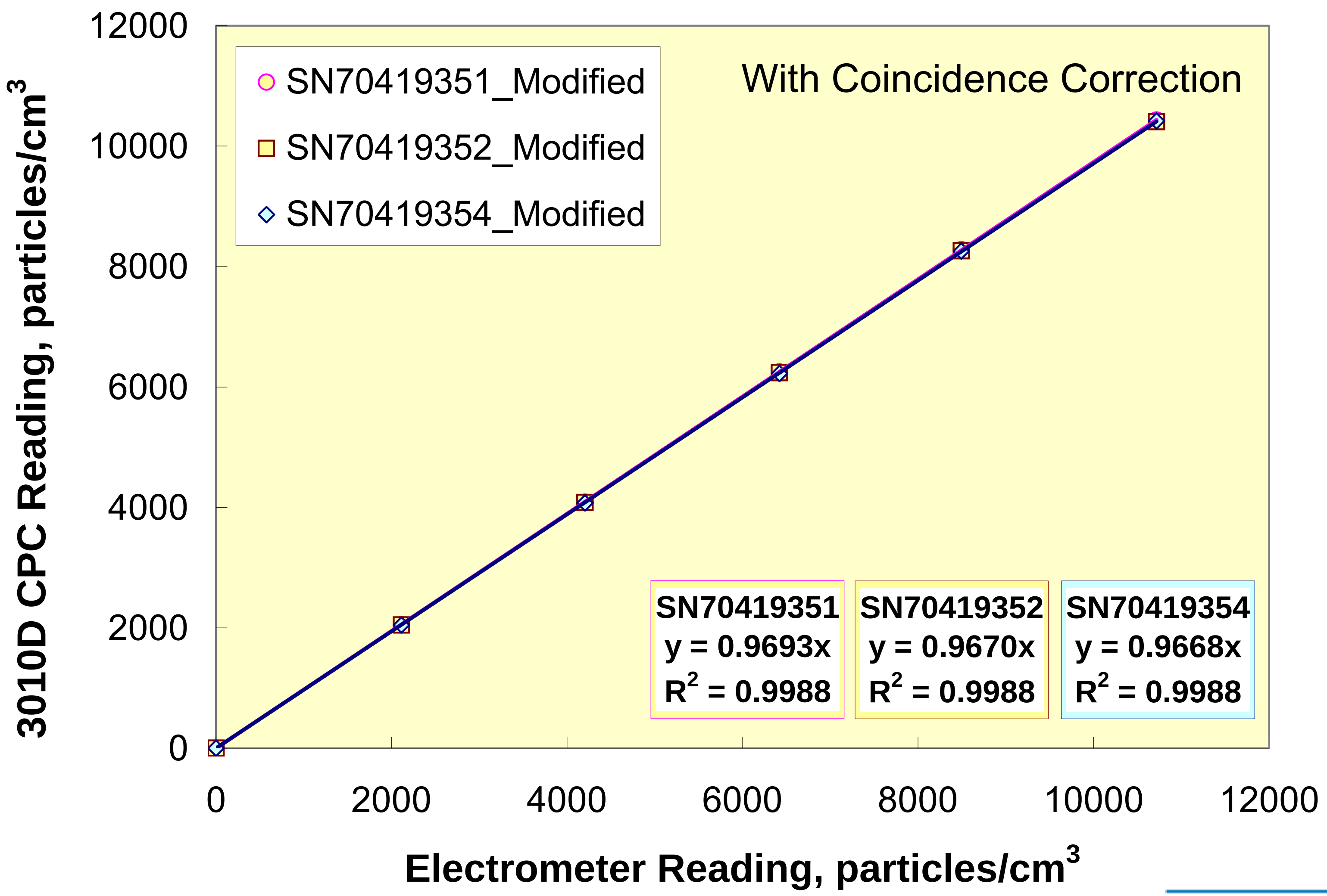
	SN2454_M	SN2460_M	SN70419351_M	SN70419354_M	SN70419352_M	Size Range	PMP Range
D10, nm	15.9	16.2	15.8	16.4	16.5	16.1 ± 0.4	16 ± 1
D25, nm	17.9	18.2	17.9	18.5	18.4	18.2 ± 0.3	18 ± 2
D50, nm	21.3	21.6	21.5	22.1	21.9	21.7 ± 0.4	23 ± 3
D90, nm	34.9	35.3	33.4	33.9	34.8	34.3 ± 1.0	37 ± 4

PMP - Comparison w/ Diffusion Screen



Model 3010D CPC has sharper efficiency curve than standard 3010 CPC with one diffusion screen in front of the inlet

PMP CPC - Linearity Response



Slope = 0.967 to 0.969

R^2 > 0.998

Conclusions

- CPC calibration required for regulatory testing
- Electrospray, DMA + Electrometer combination offers NIST traceable, independent method
  - Capable of calibrating smallest particle size detection limit, particle counting efficiency & linearity response
- Standard 3010 CPCs shows
  - Smallest particle size detection is 9 to 10 nm
  - Linear response with slope of 0.95-0.97 & $R^2 > 0.998$
- Model 3010D CPCs provide secondary safety factor to exclude nucleation mode particles
  - Smallest particle size detection adjusted to >20 nm
  - Linear response with slope of ~0.97 & $R^2 > 0.998$
  - Much sharper efficiency curve than CPCs fitted with diffusion screens

Final Slide

Thank you for your attention !

Questions ?

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