Comparison of Primary and Secondary PNC-Calibration with Electrosprayed Poly-Alpha-Olefin Particles and Flame-Generated Soot Particles

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Overview

- Calibration with electrosprayed PAO “Emery® oil”
- Calibration with flame soot
- Sources for errors
- Recommendations for good laboratory practice
- Summary and conclusions

PMP-PNC Calibration Principle

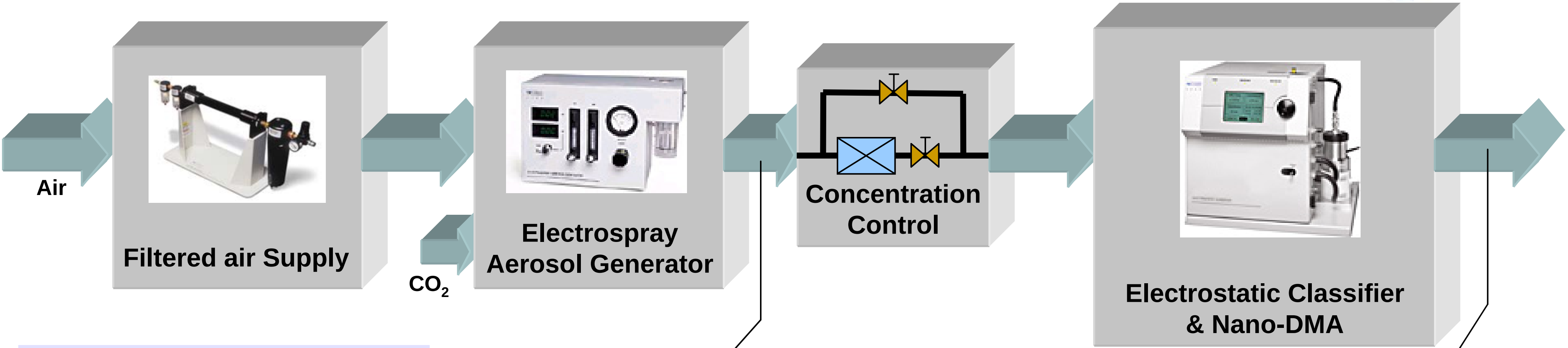
1. Calibration of PNCs against a reference electrometer is used as traceable primary calibration
2. A reference CPC calibrated against a reference electrometer is a valid, traceable transfer standard (secondary calibration)
3. While method (1) needs more attention and expertise to reach a low level of measurement uncertainty, method (2) is often easier applicable in the field.

Key Influences

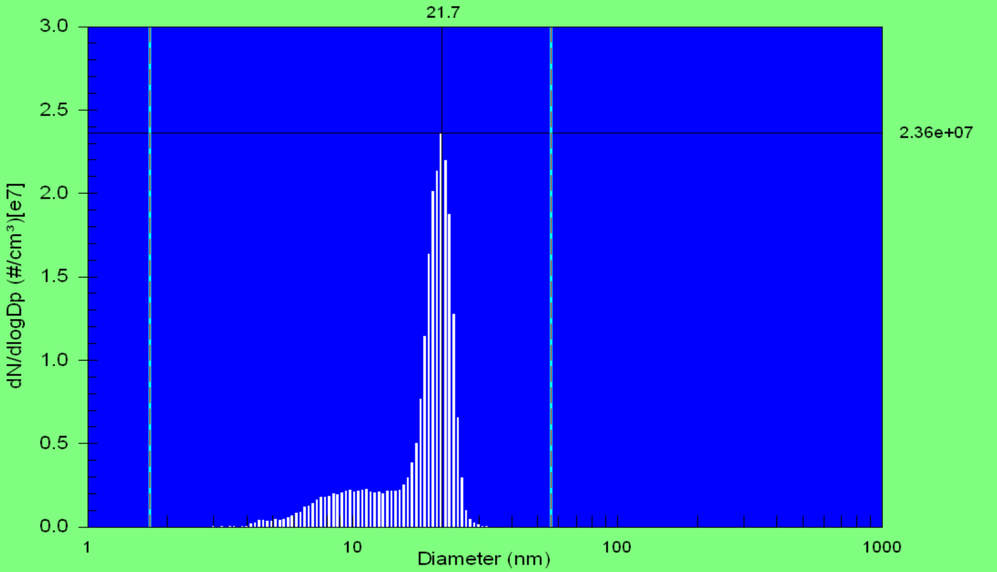
- Multiple charges bias the electrometer response
- Multiple charges cause a multimodal calibration aerosol, which biases efficiency calibration
- Non-spherical calibration aerosol adds requirement of morphological stability
  - Repeatable and reproducible mobility equivalent diameter is important

Therefore: the ideal calibration aerosol is monodisperse, spherical and singly charged.

PAO Calibration Aerosol



Raw PAO Particles
for 23 nm Calibration

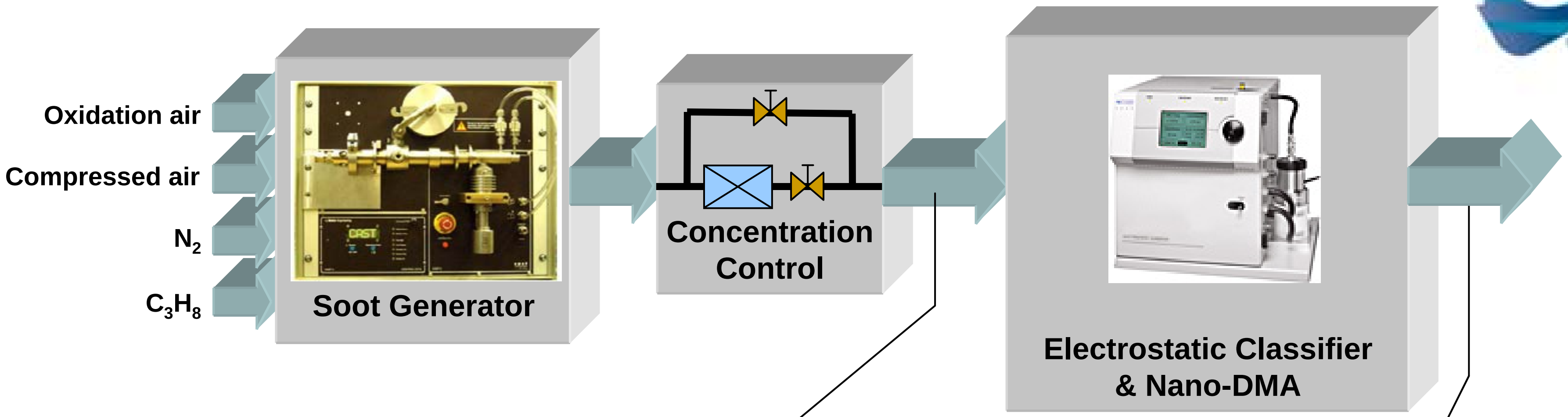


Calibration Particles	
22 nm - single charge	99.919%
32 nm - double charge	0.081%
40 nm - triple charge	0.000001%

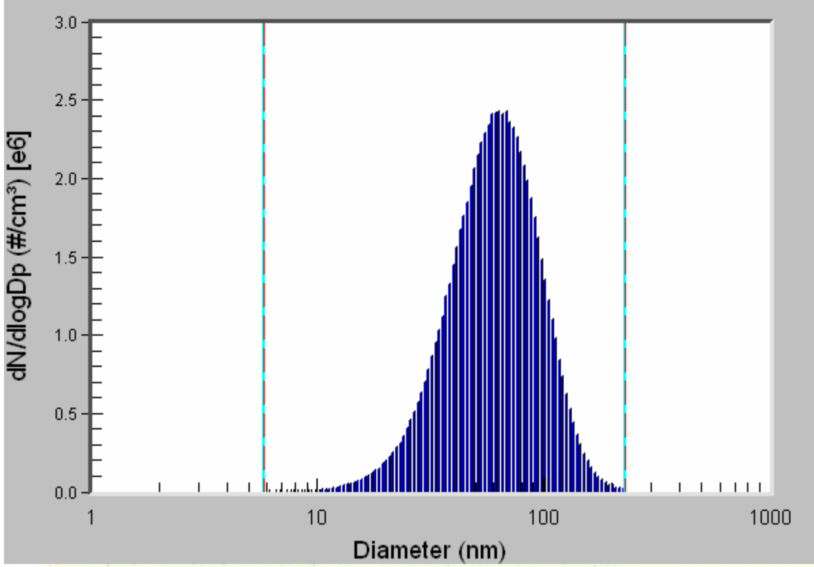
Monodisperse (GSD < 1.05)
Spherical
Singly charged

> Ideal for calibration

Flame Soot Calibration Aerosol



Raw flame soot particles
Example: 61nm (σ_g = 1.59)

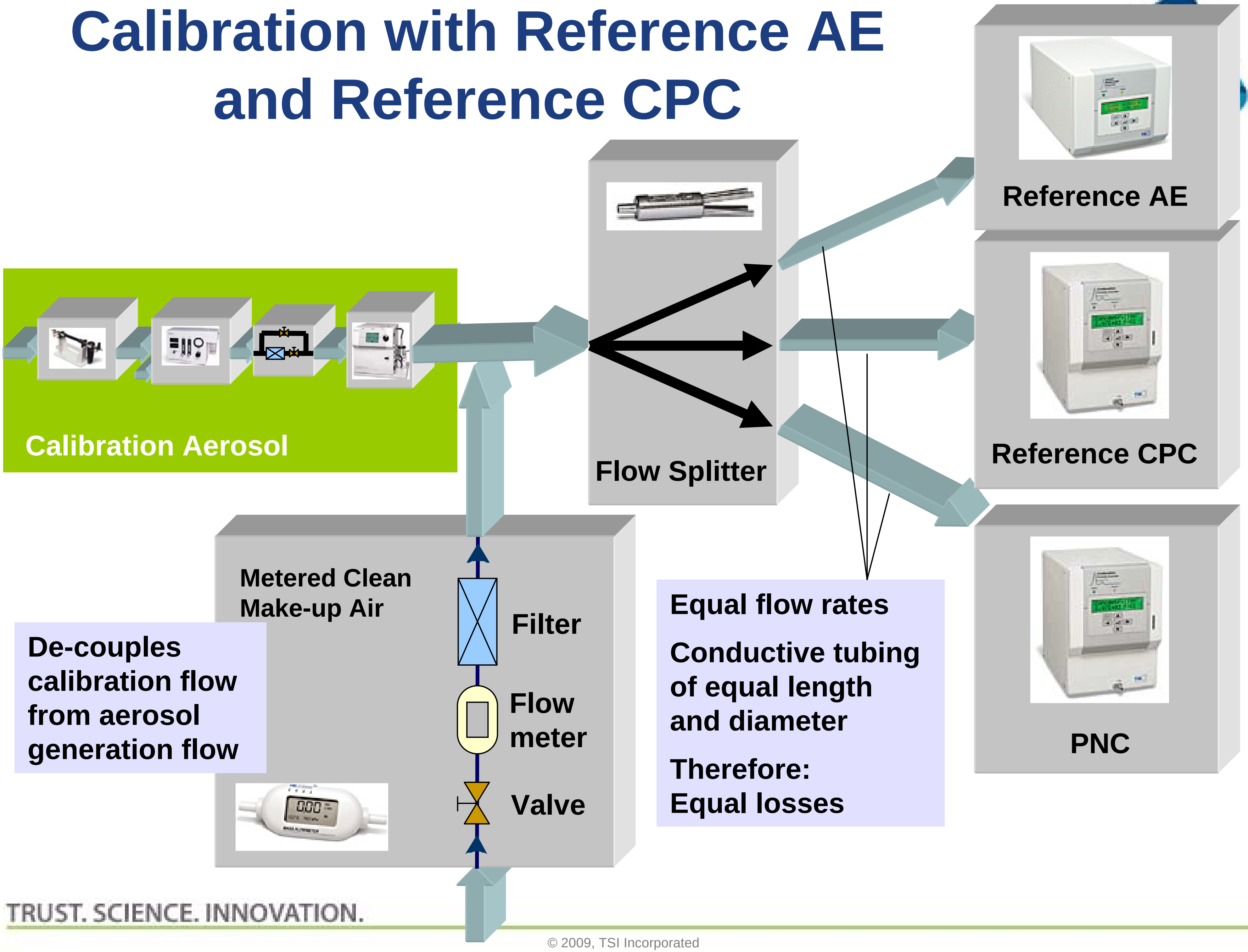


Calibration Particles	
22 nm - single charge	90.868%
32 nm - double charge	8.663%
40 nm - triple charge	0.47%

Multimodal
Non-spherical (agglomerates)
Multiply charged

> Corrections must be applied

Calibration with Reference AE and Reference CPC



Calibration: Reference AE versus Reference CPC

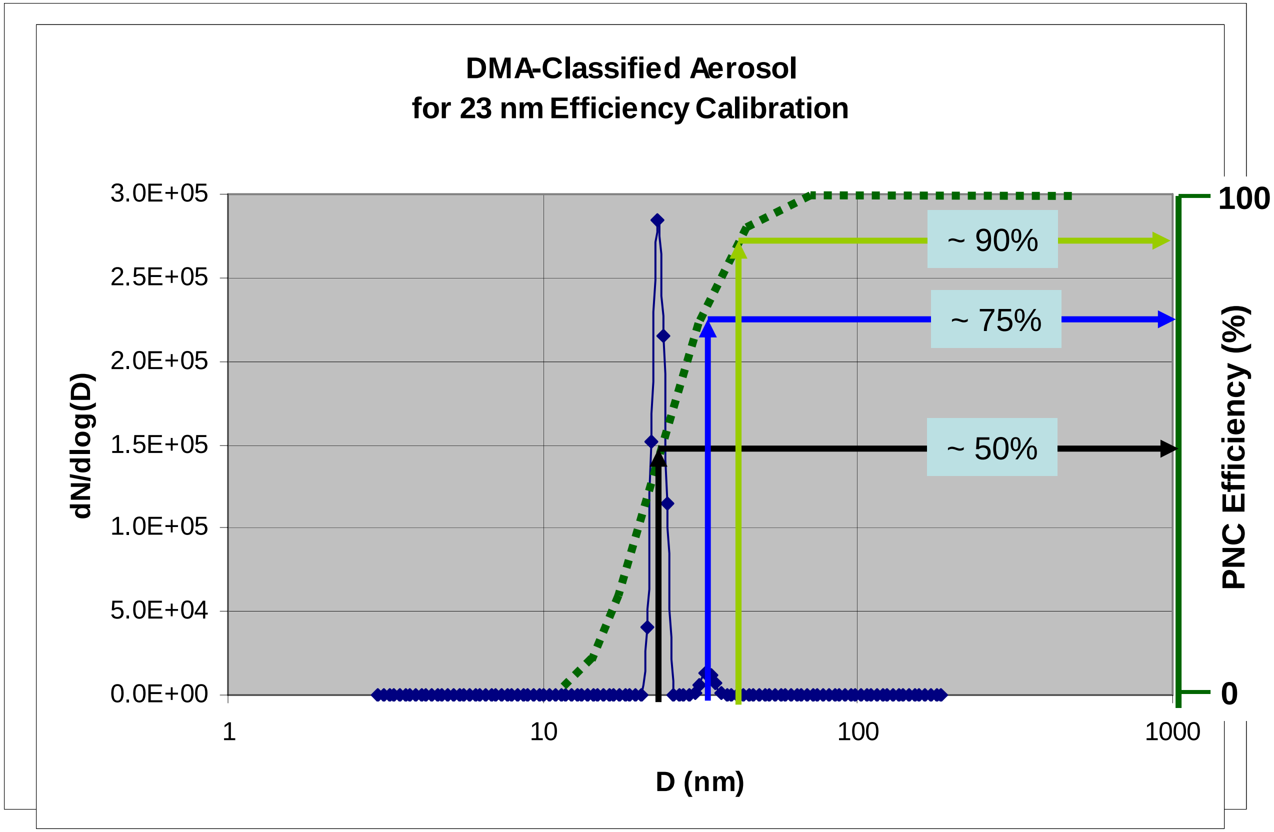
Reference AE

Reading must be corrected if particles carry multiple charges; efficiency curve calibration result must be corrected if particles have more than one mode.

Reference CPC

Calibration result for efficiency curve calibration must be corrected if calibration particles have more than one mode (e.g. due to multiple charges).

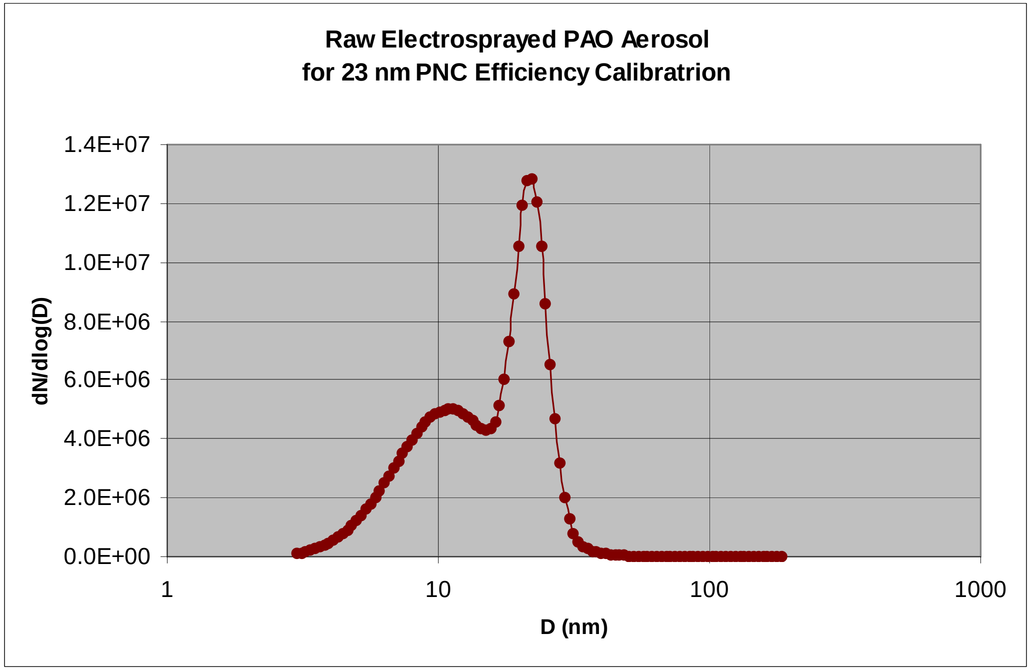
Efficiency Calibration

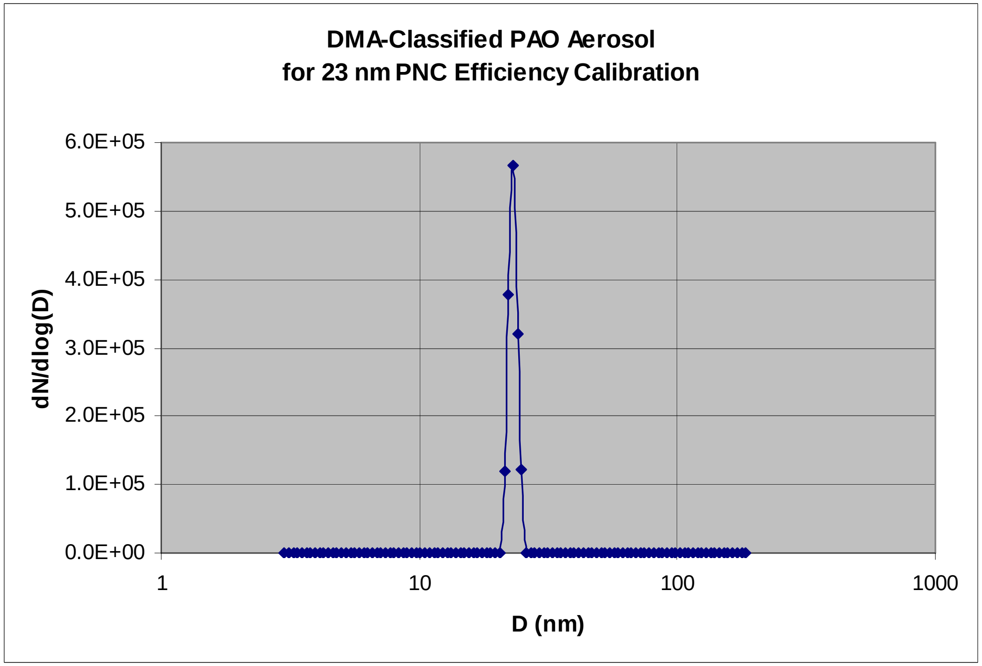


- For correction of multiple charge effects, an effciency curve must be assumed for the calibrant PNC
- Calibration with reference CPC requires multiple mode correction
- Reference electrometer current must in addition be corrected for multiple charges on classified particles

Example: Flame soot, D_{50} = 55 nm, GSD = 1.6

PNC Efficiency Calibration with 23 nm Electrosprayed PAO



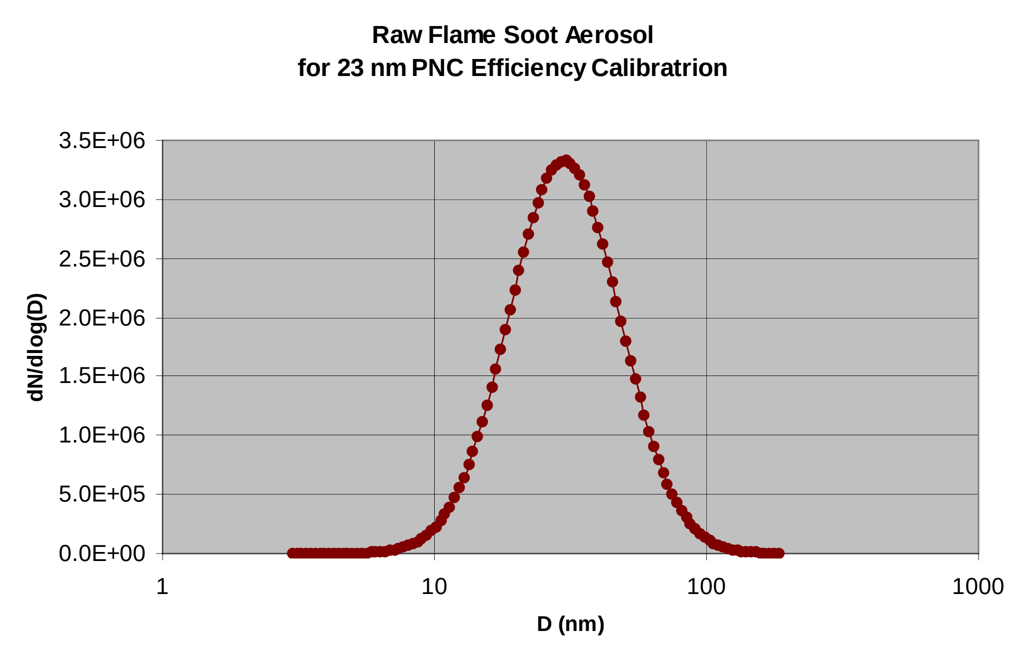


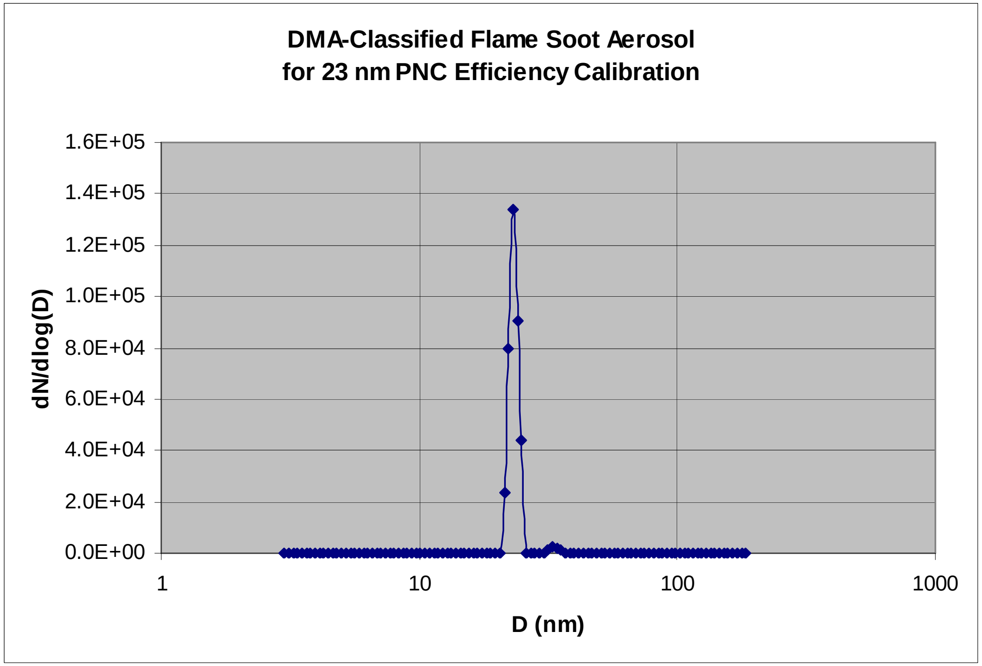
	Elementary Charges			Correction (Efficiency)
	+	++	+++	
D (nm)	23	33	42	
CPC: % of total number	99.93%	0.07%	0.00%	**-0.03%**
Electrometer: % of total current	99.86%	0.14%	0.00%	**0.03%**

Expected calibration errors are insignificant.

- Uncorrected calibration result will be slightly too high (correction –0.03%) for calibration against reference CPC
- Uncorrected calibration result will be slightly too low (correction +0.03%) for calibration against reference electrometer

PNC Efficiency Calibration with 23 nm Flame Soot



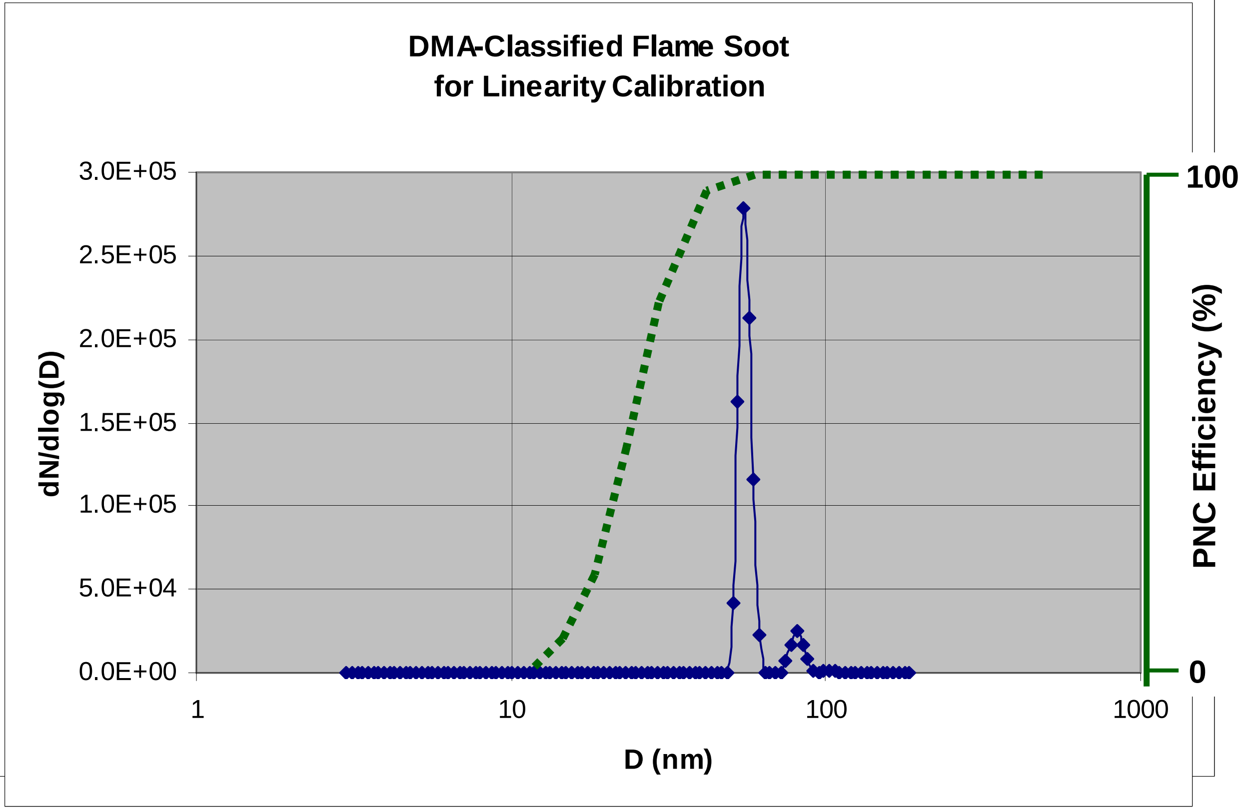


	Elementary Charges			Correction (Efficiency)
	+	++	+++	
D (nm)	23	33	42	
CPC: % of total number	98.24%	1.76%	0.00%	**-0.88%**
Electrometer: % of total current	96.54%	3.46%	0.01%	**0.87%**

Expected calibration errors are small, approximately 1%

- Uncorrected calibration result will be too high (correction –0.88%) for calibration against reference CPC
- Uncorrected calibration result will be too low (correction +0.87%) for calibration against reference electrometer

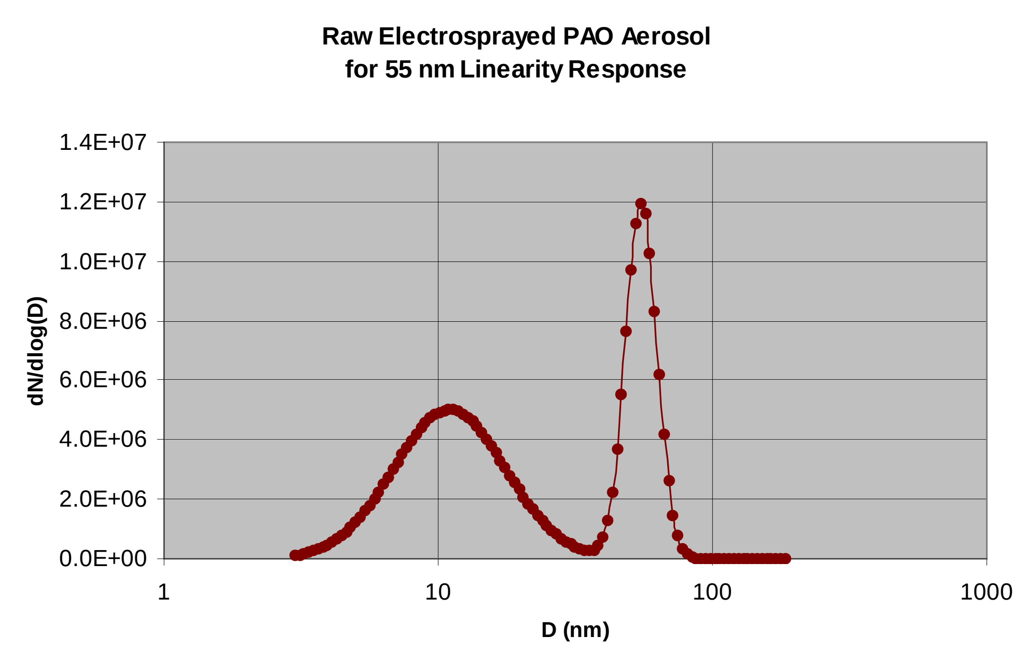
Linearity Response Calibration

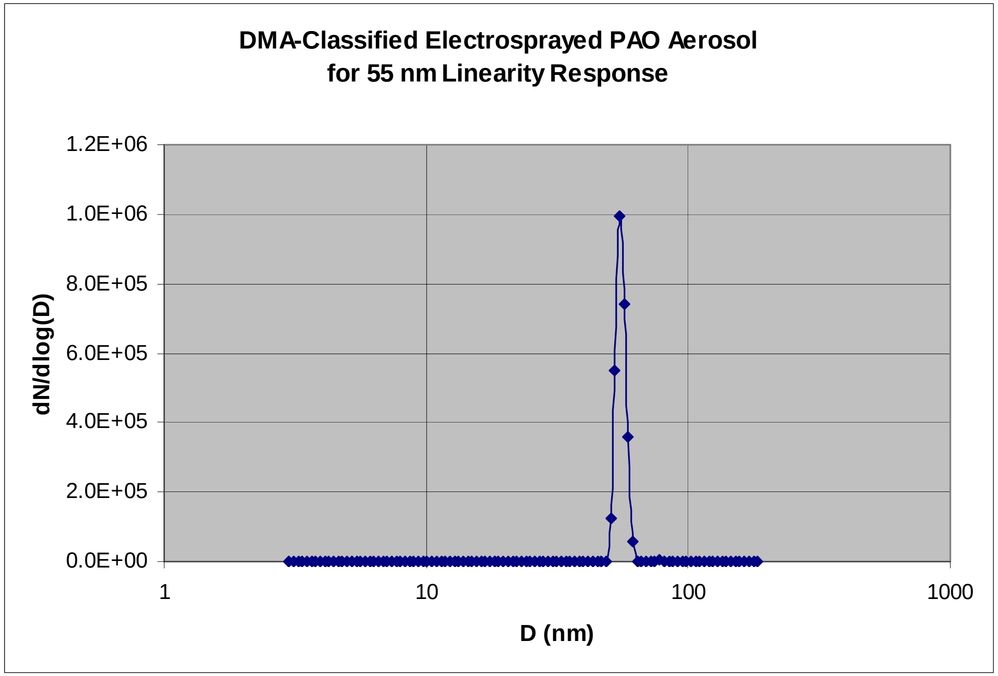


Example: Flame soot, D_{50} = 55 nm, GSD = 1.6

- Multiple charges of classified particles do not bias the calibrant PNC response as long as its counting effciency is near 100%
- Calibration with reference CPC does not require multiple mode correction
- Reference electrometer current must be corrected for multiple charges on classified particles

PNC Linearity Response with 55 nm Electrosprayed PAO





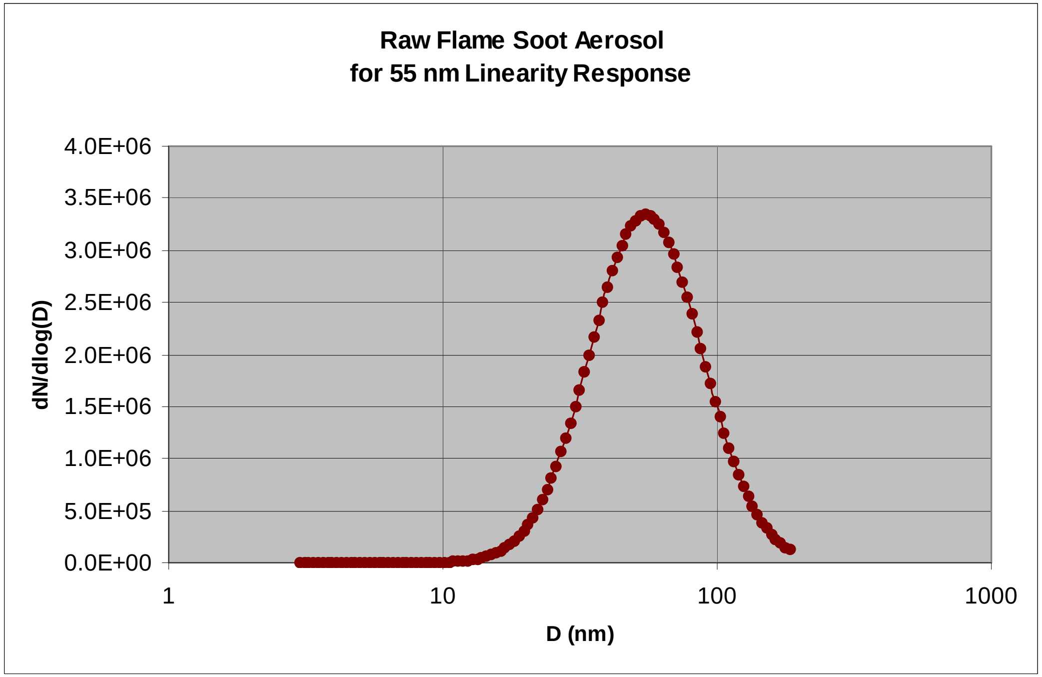
	Elementary Charges			Correction
	+	++	+++	(Linearity)
D (nm)	55	78	95	
CPC: % of total number	99.77%	0.23%	0.00%	**0.00%**
Electrometer: % of total current	99.54%	0.46%	0.00%	**0.23%**

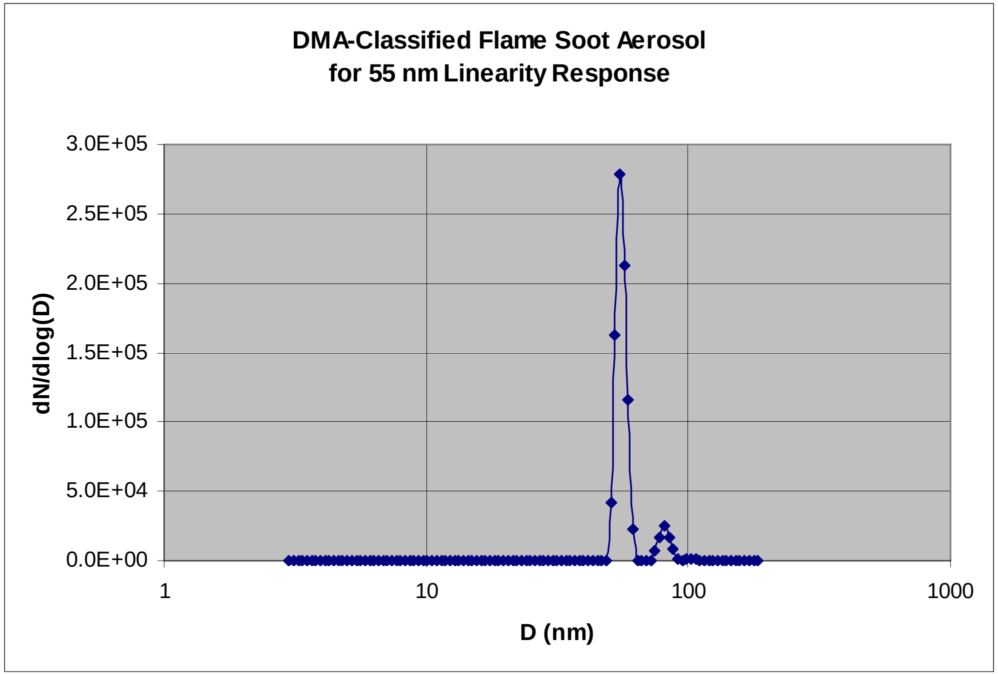
Expected calibration errors are very small

-Linearity response measurement against reference CPC is unbiased by multiple charges

-Uncorrected reference electrometer reading will be slightly too high (correction -0.23%) and resulting linearity response will be slighty too low (correction +0.23%)

PNC Linearity Response with 55 nm Flame Soot





	Elementary Charges +	++	+++	Correction (Linearity)
D (nm)	55	81	102	
CPC: % of total number	91.37%	8.20%	0.42%	**0.00%**
Electrometer: % of total current	83.79%	15.04%	1.17%	**9.05%**

Expected calibration errors:

-Linearity response measurement against reference CPC is unbiased by multiple charges

-Uncorrected reference electrometer reading will be significantly too high (correction -8.30%) while the measured linearity response is too low (correction +9.05%)

Remember: Key Influences

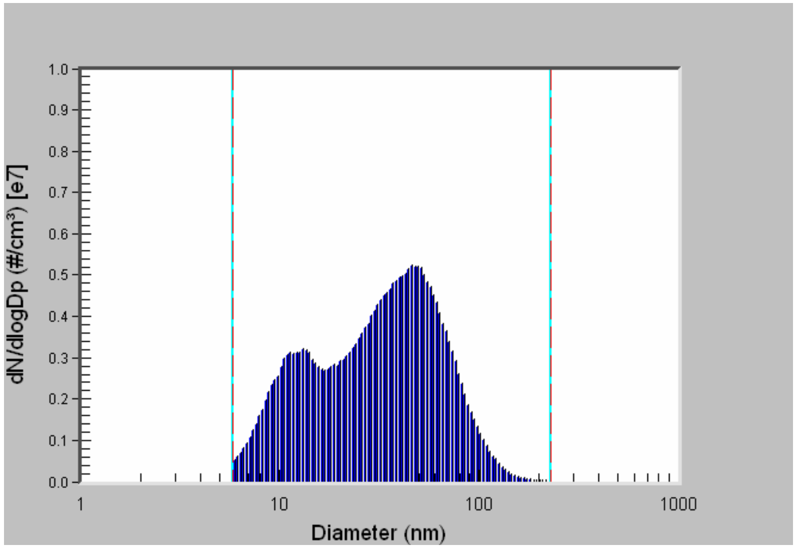
- Multiple charge correction requires the knowledge of the charge distribution.
  - Three possible solutions:
    1. Ensure charge equilibrium through appropriate charge neutralization
    2. Measure the charge distribution before correction
    3. Eliminate particles with more than 1 charge by using a 2nd DMA

Charge Equilibrium

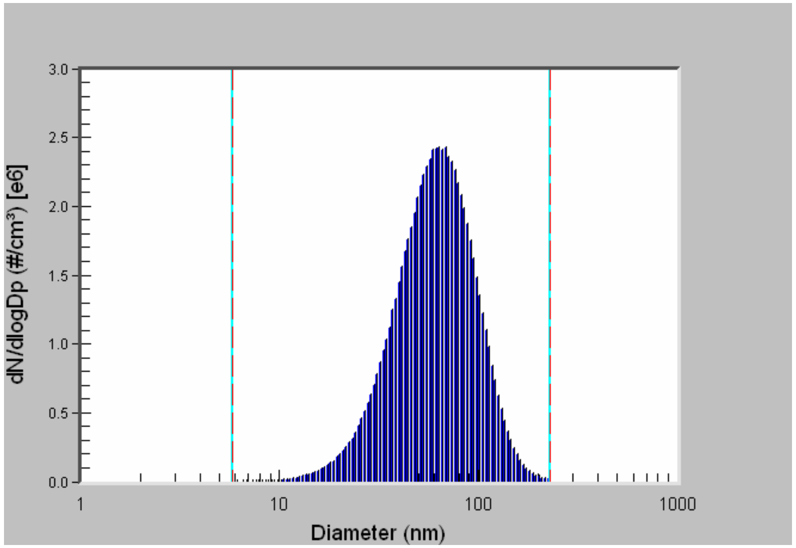
- Equilibrium charge distribution on loose agglomerates (soot) differs from the well known charge distribution on spherical particles (PAO)
  - This adds measurement uncertainty
  - Repeatability and reproducibility of the particle morphology is required.
- Pre-charged, high concentration flame soot particulates can be difficult to neutralize.

Soot Charge Equilibrium

- How sure can we be that soot calibration aerosol has reached charge equilibrium?



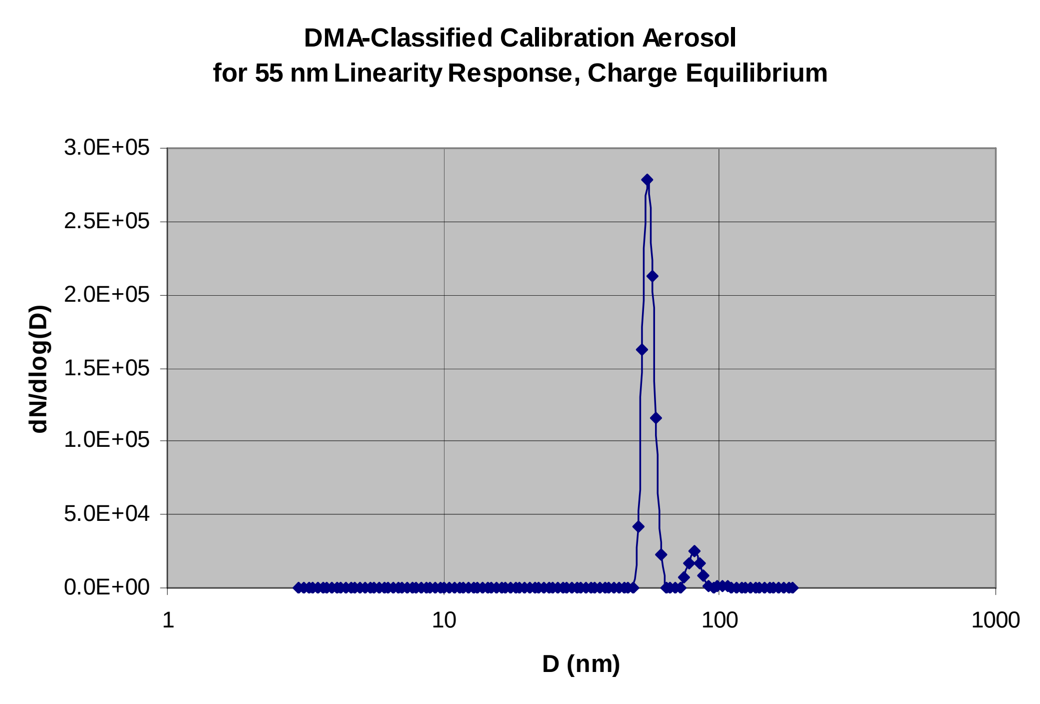
High soot aerosol concentration and 1 neutralizer TSI model 3077: *SMPS measurement shows that charge equilibrium was not reached*

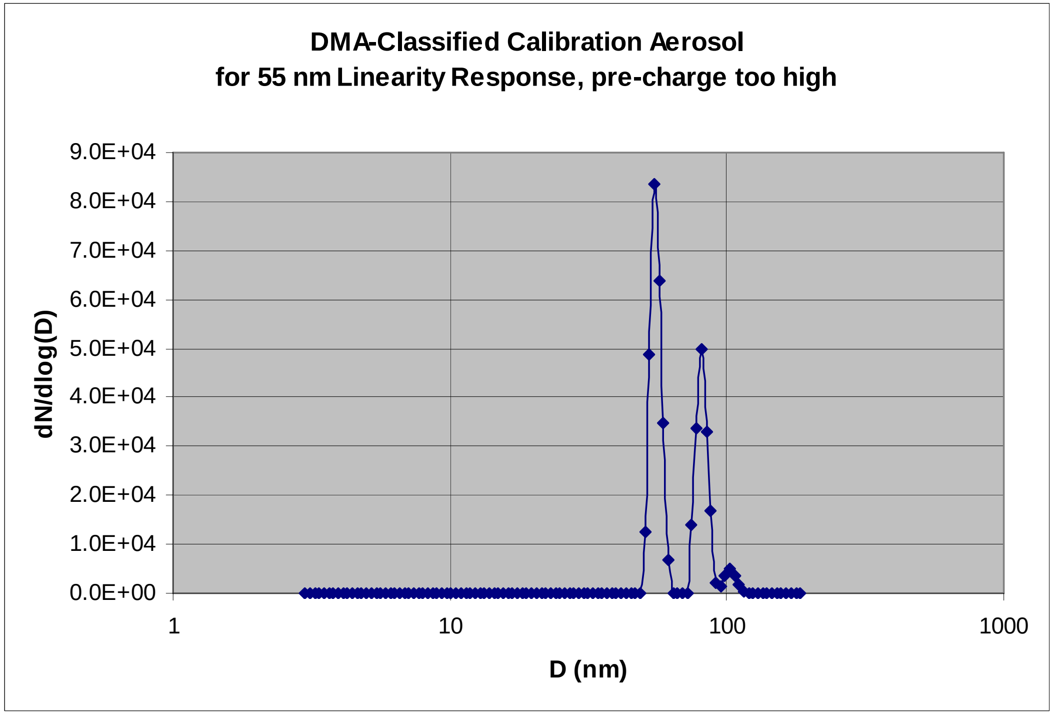


Diluted soot aerosol and neutralizers TSI models 3077 and 3012 in series:
Charge equilibrium was reached

If the poorly neutralized aerosol (left hand side) is used for calibration, assuming charge equilibrium for correction can lead to approximately 50% relative error.

Highly Pre-Charged Calibration Aerosol





	Elementary Charges +	++	+++	Correction (Linearity)
D (nm)	55	81	102	
CPC: % of total number	91.37%	8.20%	0.42%	**0.00%**
Electrometer: % of total current	83.79%	15.04%	1.17%	**9.05%**

	Elementary Charges +	++	+++	Correction (Linearity)
D (nm)	55	81	102	
CPC: % of total number	60.23%	36.05%	3.72%	**0.00%**
Electrometer: % of total current	41.97%	50.24%	7.79%	**43.50%**

If this situation remains undiscovered, the assumption of charge-equilibrium will result in serious errors!

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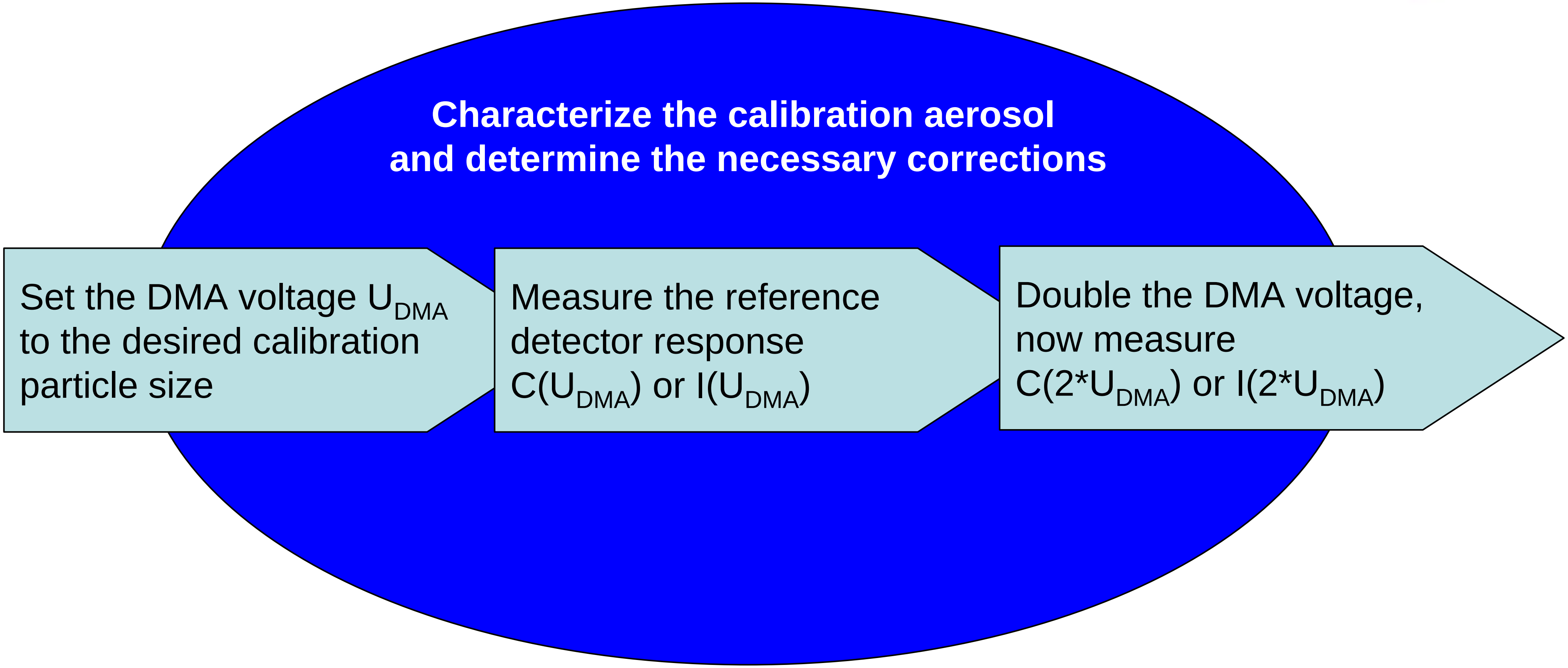
Recommended Practice

The „Double Voltage Test“



This simple routine helps to increase calibration quality by eliminating a source for errors.

GLP for PNC Calibration

- Calibration with PAO
  - Verify that the raw calibration aerosol has a narrow size distribution. The measured number concentration or electrometer current should decrease to 5% or less of the original value when doubling the DMA voltage.

- Calibration with flame soot
  - Reducing the soot aerosol to only singly charged particles with a second DMA in series makes the calibration results reliable.
  - Measurement of the fraction of multiple charged particles with a tandem DMA setup (classifying DMA followed by measuring SMPS) and applying corrections is an appropriate option, too. Check the validity of corrections regularly with the “double voltage test”.
  - However, the uncertainty due to a poorly defined relation between mobility diameter and soot particle size remains for the efficiency calibration
    - Reproducibility and repeatability of the morphology of calibration soot needs attention.

Summary and Conclusions

- Electrosprayed and DMA-classified PAO particles are ideal calibration particles
- Raw particles with wider size distributions (e.g. flame soot) can be used for calibration
  - Multiple modes and multiple charges must be characterized to establish the necessary corrections
  - After the characterization, a simple check (double DMA voltage) can prove that the corrections are still valid
- The physical and chemical properties of the calibration particle material may influence the calibration result
  - Different particle material can yield different detection efficiency curves
- ISO/TC 24/SC 4/WG 12 actually writes a CPC calibration standard addressing these issues

Thank You Very Much For Your Attention!

Any Questions?