PMP

PNC Calibration

Recent Experiences

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PMP Meeting, London, 30 March 2009

Objective

- During the last year, we were several times faced to situations where PNC calibrations with Emery Oil and soot disagreed substantially.
- Problems with the multiple charge correction for soot particles were found as the main source of confusion.
- The following example (from joint measurements with Volkswagen AG at our lab in Aachen) explains the difficulties.

Primary 23 nm PNC Efficiency Calibration Assuming Charge Equilibrium

23 nm PNC Efficiency Calibration with Reference Electrometer and CAST Soot

Number of charges n	1+	2+	3+	
Corresponding DMA voltage	V1	2*V1	3*V1	< This is always valid
C (1/cm³)	4.17E+03	1.62E+04	3.47E+04	< These are measured values
C n+ / C 1+ (%)		388.71%	830.41%	< Wide size distribution: Concentration of larger particles will always be high
Mobility equivalent diameter (nm)	23.3	33.3	41.2	< This is a true diameter for spheres only
Fraction p of C with n charges		**0.0116**	**1.10E-05**	**< DO WE USE THE RIGHT CHARGE DISTRIBUTION MODEL FOR SOOT?**
Resulting C*p for calibration	3.98E+03	1.88E+02	3.81E-01	< This is only valid if p is correct
Total C measured by PNC		2.12E+03		
Expected electrometer over-reading		9.47%		< This is only valid if p is correct
Expected calibration error		**-2.60%**		**Error correction requires assumption of an efficiency curve** **< Error correction will only be valid if:** **1) assumed charge distribution is valid for soot** **2) charge equilibrium was reached before the DMA**

23 nm PNC Efficiency Calibration with Reference Electrometer and Electrospray Emery Oil

Number of charges n	1+	2+	3+	
Corresponding DMA voltage	V1	2*V1	3*V1	< This is always valid
C (1/cm³)	4.08E+04	1.89E+03	2.60E+01	< These are measured values
C n+ / C 1+ (%)		4.65%	0.06%	**< Very low concentration of larger particles reduces uncertainty**
Mobility equivalent diameter (nm)	23.3	33.3	41.2	< geometric diameter for spheres
Fraction p of C with n charges		**0.0116**	**1.10E-05**	**< CHARGE DISTRIBUTION WELL KNOWN FOR SPHERES**
Resulting C*p for calibration	4.07E+04	2.20E+01	2.86E-04	
Total C measured by PNC		2.04E+04		
Expected electrometer over-reading		0.11%		
Expected calibration error		**-0.03%**		**< This error is insignificant**

Secondary 23 nm PNC Efficiency Calibration Assuming Charge Equilibrium

23 nm PNC Efficiency Calibration with Reference CPC and CAST Soot				
Number of charges n	1+	2+	3+	
Corresponding DMA voltage	V1	2*V1	3*V1	< This is always valid
C (1/cm³)	4.17E+03	1.62E+04	3.47E+04	< These are measured values
C n+ / C 1+ (%)		388.71%	830.41%	< Wide size distribution: Concentration of larger particles will always be high
Mobility equivalent diameter (nm)	23.3	33.3	41.2	< This is a true diameter for spheres only
Fraction p of C with n charges		**0.0116**	**1.10E-05**	**< DO WE USE THE RIGHT CHARGE DISTRIBUTION MODEL FOR SOOT?**
Resulting C*p for calibration	3.98E+03	1.88E+02	3.81E-01	< This is only valid if p is correct
Total C measured by Ref CPC (100% Eff)		4.17E+03		
Total C measured by PNC		2.12E+03		
Expected calibration error		**1.81%**		**< This error is less critical (compared to primary electrometer calibration)** Error compensation requires assumption off efficiency curve

23 nm PNC Efficiency Calibration with Reference CPC and Electrospray Emery Oil				
Number of charges n	1+	2+	3+	
Corresponding DMA voltage	V1	2*V1	3*V1	< This is always valid
C (1/cm³)	4.08E+04	1.89E+03	2.60E+01	< These are measured values
C n+ / C 1+ (%)		4.65%	0.06%	**< Very low concentration of larger particles reduces uncertainty**
Mobility equivalent diameter (nm)	23.3	33.3	41.2	< geometric diameter for spheres
Fraction p of C with n charges		**0.0116**	**1.10E-05**	**< CHARGE DISTRIBUTION WELL KNOWN FOR SPHERES**
Resulting C*p for calibration	4.07E+04	2.20E+01	2.86E-04	
Total C measured by Ref CPC (100% Eff)		4.08E+04		
Total C measured by PNC		2.04E+04		
Expected calibration error		**0.02%**		**< This error is insignificant**

Primary PNC Linearity Calibration Assuming Charge Equilibrium

PNC Linearity Calibration with Reference Electrometer and CAST Soot				
Number of charges n	1+	2+	3+	
Corresponding DMA voltage	V1	2*V1	3*V1	< This is always valid
C (1/cm³)	6.73E+04	4.95E+04	2.39E+04	< These are measured values
C n+ / C 1+ (%)		73.60%	35.54%	< Wide size distribution: Concentration of larger particles will always be high
Mobility equivalent diameter (nm)	63.8	93.8	118.7	< This is a true diameter for spheres only
Fraction p of C with n charges		0.1177	0.0132	**< DO WE USE THE RIGHT CHARGE DISTRIBUTION MODEL FOR SOOT?**
Resulting C*p for calibration	6.11E+04	5.83E+03	3.15E+02	< This is only valid if p is correct
Total C measured by PNC		6.73E+04		
Total C (1+) measured by AE		7.37E+04		**< This is only valid if p is correct and charge equilibrium was reached**
Resulting Calibration error		**-8.76%**		

PNC Linearity Calibration with Reference Electrometer and Electrospray Emery Oil				
Number of charges n	1+	2+	3+	
Corresponding DMA voltage	V1	2*V1	3*V1	< This is always valid
C (1/cm³)	4.20E+04	2.21E+03	5.75E+02	< These are measured values
C n+ / C 1+ (%)		5.27%	1.37%	**< Very low concentration of larger particles reduces uncertainty**
Mobility equivalent diameter (nm)	55.1	80.4	100.9	< geometric diameter for spheres
Fraction p of C with n charges		0.0937	0.007	**< CHARGE DISTRIBUTION WELL KNOWN FOR SPHERES**
Resulting C*p for calibration	4.18E+04	2.07E+02	4.03E+00	
Total C measured by PNC		4.20E+04		
Total C (1+) measured by AE		4.22E+04		
Resulting Calibration error		**-0.51%**		**< VERY SMALL CORRECTION REDUCES UNCERTAINTY**

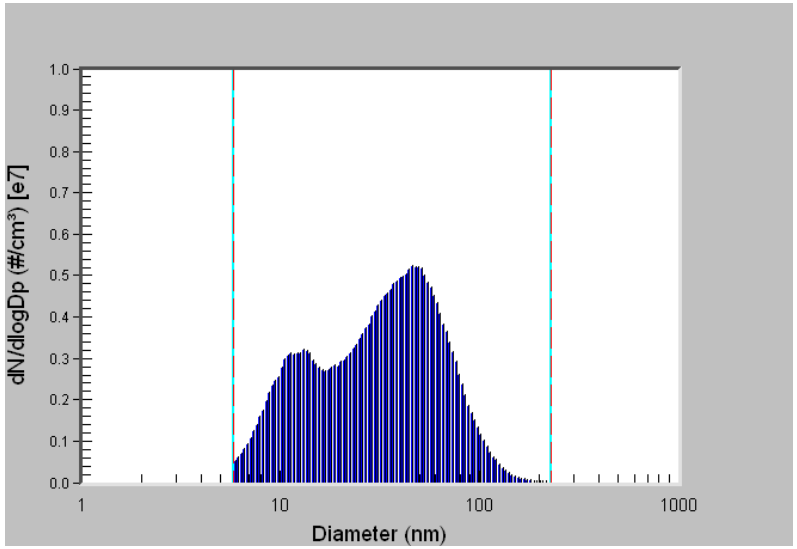
Note: Secondary linearity calibration with reference CPC is not biased by multiple charges

Charge Equilibrium

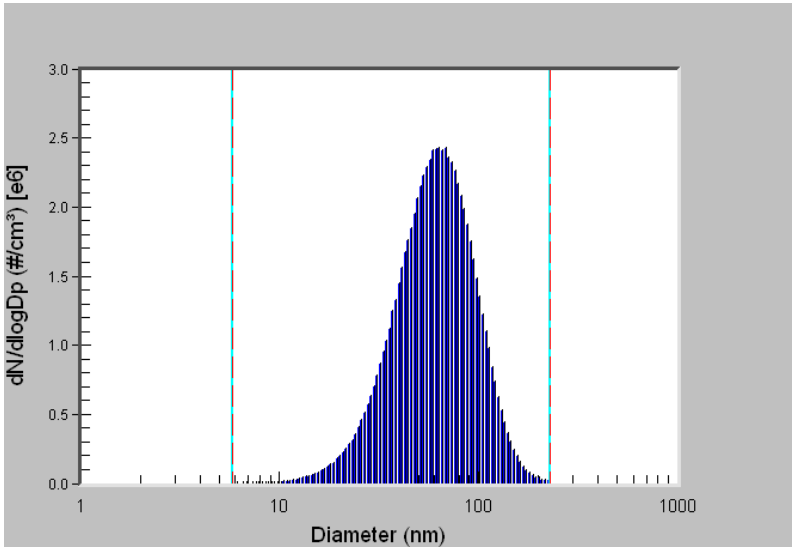
- Pre-charged, high concentration soot particulates are difficult to neutralize.
- Multiple charge correction for primary PNC calibration is typically based on the assumption of charge equilibrium
- We have seen cases where non-charge equilibrium conditions of soot particulates caused very large calibration errors.

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 will lead to approximately 50% relative error.

Possible Improvements if Soot is Used for Calibration

- A soot particle generator should always be set such that
  - The D_{50} of the soot size distribution is smaller than the size selected by the DMA
  - The GSD of the soot size distribution should be as small as possible
  - The total soot particle number concentration entering the DMA should be lower than 10^6 cm^{-3}
- Reducing the soot aerosol to only singly charged particles with a second DMA in series makes the calibration results match sufficiently well.
- Measurement of the fraction of multiple charged particles with a tandem DMA setup (classifying DMA followed by measuring SMPS) is an option, too.
- However, the uncertainty due to a poorly defined relation between mobility diameter and soot particle size remains for the efficiency calibration
  - What do we know about reproducibility and repeatability of the morphology of calibration soot?

Conclusions - I

- For primary PNC *efficiency and linearity* calibration with an aerosol electrometer, we strongly recommend to use electrosprayed Emery oil particles to minimize the measurement uncertainty
- If a calibration aerosol with large fractions of multiple charged particles (e.g. CAST soot) is used, the charge state of the calibration aerosol should be **measured**.
  - *In this case, assuming charge equilibrium for multiple charge correction is not sufficient and can lead to large errors.*

Conclusions - II

- For secondary PNC *efficiency* calibration with a reference CPC, multiple charged particles are less critical, but the calibration error still increases with increasing particle charge.
- For secondary PNC *linearity* calibration with a reference CPC, multiple charged particles do not result in errors.
- Without the proven low measurement uncertainty of electrospray/Emery oil calibration, achieving robust calibration results becomes more difficult.

Thank you very much for your attention!