Calibration and Validation of PMP compliant Condensation Particle Counters and Dilution Systems using Combustion Aerosol Standard

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Motivation:

The homologation procedure for Diesel vehicles for the Euro 5+ stage in 2011 most likely will be extended to include the measurement of particle number emissions. The measurement will follow the procedure defined by the PMP (Particle Measurement Programme) group established by the United Nations Economic Commission for Europe (UN-ECE). In order to built up a traceable measurement chain, in a first step <step 1> investigations with respect to the calibration and validation of the Condensation Particle Counter (CPC) are necessary. In a second step <step 2> the calibration of the volatile particle remover (VPR) using the concept of the particle concentration reduction factor (fr) has to be examined with respect to the thermal stability of the aerosol material used.

<Step 1> PNC Calibration with Combustion Soot Particles

•Experimental Setup
The calibration of the CPC shall be traceable to a standard calibration method by comparing the response of the CPC under calibration with that of a calibrated aerosol electrometer (AE) when simultaneously sampling electrostatically classified calibration particles by means of a Differential Mobility Analyzer (DMA).
For the sake of comparability the calibration aerosol material should be as similar as possible to what is measured in reality. Because of that combustion soot particles are prefered. In the laboratory one way of generating soot particles is to use a CAST (Combustion Aerosol Standard, Matter Engineering AG) producing propane flame combustion soot particles in the desired particle number concentration regime.

•Results
At first, validation attempts supplied unsatisfactory results, which imply correlation coefficients (R^2) at 0,998 but regression gradient in the range of 0.65 to 0.75.
In order to reduce a potential multiple-charge-effect the size distribution of the CAST-aerosol was optimized by shifting the particle size distribution towards smaller size (CMD = 28 nm). With this size distribution the regression gradient was raised up to 0.85.
Figure 1 shows the development of the regression gradients by
- the improvement of the aerosol (shifting the size distribution to smaller size),
- the consideration of the multiple loads,
- the “cross cut”

• Multiple charge effects:
Multiple charged aerosol particles are assumed theoretically and exist in reality. In fact, between the theoretically determined and the measured amount of multiple charges exists a bigger difference as theoretically expected, which was shown by measuring multiple charges by means of t-DMA setup. However, measuring the multiple charges before calibration is started makes the calibration time consuming and complicated.

•Solution: The cross cut
A way out of this cul-de-sac is to make sure that there are no multiple charged particles in the aerosol. We used the set up is shown in figure 2. The raw CAST Aerosol was fed into the first DMA without prior neutralization and cut at a diameter of 37nm. Now, the Aerosol consists of 37nm singly charged, 55nm double charged and 80nm triply charged Particles. In the second DMA the radioactive source neutralizes the Aerosol and cuts the 55nm singly charged particles. With this Setup the multiple charge effect can be minimized and the regression gradient could be reached as expected from the calibration certificate as delivered by the CPC manufacturer.
With this technique it is possible to generate an Aerosol of single charged particles of the desired diameter. The advantage of this procedure is the independency from the raw Aerosol. Nevertheless the results clearly show the sensitivity of the calibration of CPCs with respect to the raw Aerosol.

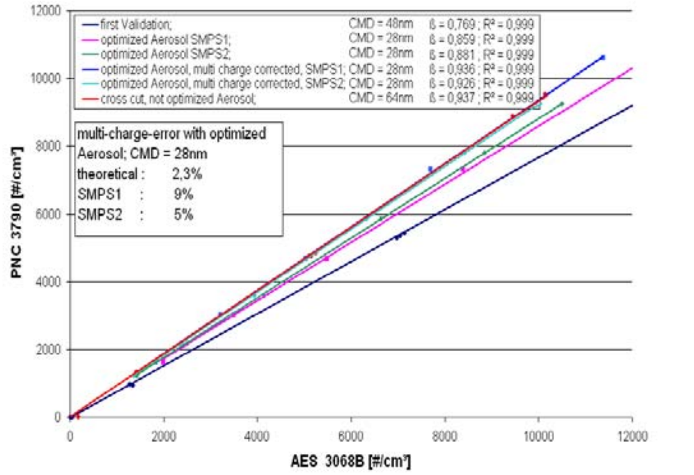

Figure 1: Different regression gradients for different CAST particles with and without multiple charge correction.

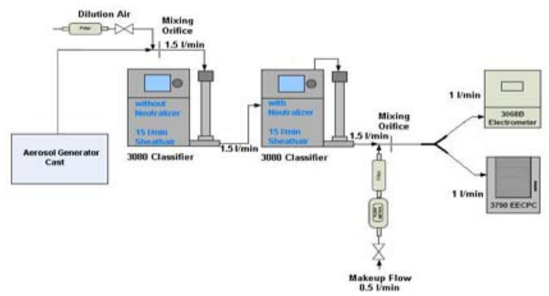

Figure 2: Setup of the cross cut method

<Step 2> VPR calibration with Combustion Soot Particles

•Procedure for the VPR calibration
• Aerosol with 100 nm particles is generated by means of a DMA
• Number concentration is just below the detection limit of the CPC (maximum calibrated concentration)
• When number concentration is stable at the outlet of the generator the concentration is measured with the calibrated CPC (*Nu100* ± *uu100* = upstream concentration and uncertainty of VPR).
• The same aerosol is fed to the inlet upstream the VPR and the concentration is measured at the outlet of the VPR with the calibrated CPC (*Nd100* ± *ud100*)
• Repeat the procedure with 50 nm particles (*Nu50* and *Nd50)* and 30nm particles (*Nu50* and *Nd50)*
• Calculate *fr*(100 nm), *fr*(50 nm), *fr*(30 nm) and *fr*= (*Nu30* + *Nu50*+ *Nu100*) / (*Nd30* + *Nd50* + *Nd100*) and their uncertainties.
•Either use the same CPC for measuring first the upstream and then the downstream concentration (Single CPC VPR Cal.) or use two CPCs and measure upstream and downstream concentration simultaneously (Double CPC VPR Cal.)

•Results
The procedure for the VPR calibration was done with both the single and the double CPC calibration procedure with two different Aerosol materials (CAST with Thermodenuder; Atomizer with NaCl solution with diffusion dryer)
The thermal stability of the aerosols was checked by measuring the size distribution prior and after the evaporation tube of the VPR. The NaCl Aerosol generated via the Atomizer and diffusion dryer showed a broadening of the size distribution and a shift to larger particle sizes, the soot Aerosol generated via CAST and Thermodenuder showed a narrowing of the size distribution but no shift with respect to the Aerosol at the inlet of the Evaporation Tube.
In dependency of the Aerosol material used the differences in the resulting *fr* were as high as 16% as shown in figure 3. The differences in fr between the Single and Double CPC Calibration method were as high as 5% as shown in figure 4.

•Conclusion:
The calibration of the VPR is on the one hand very sensitive to the aerosol material used . For the sake of comparability the calibration aerosol material should be as similar as possible to what is measured in reality. Because of that combustion soot particles are preferred. A treatment of the CAST particles is necessary to remove volatile particles prior to the inlet of the DMA. The removal of the volatiles can be done by either using a Thermodenuder or Catalytic Stripper. Furthermore the Single CPC VPR Calibration should be preferred, resulting in a better repeatability of the VPR calibration

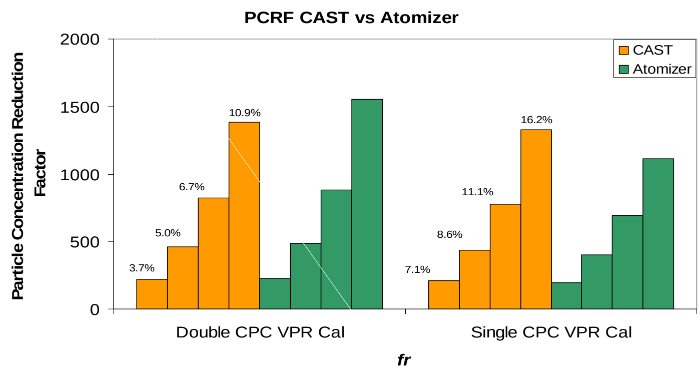

Figure 3: Calibration of the VPR with different aerosol materials

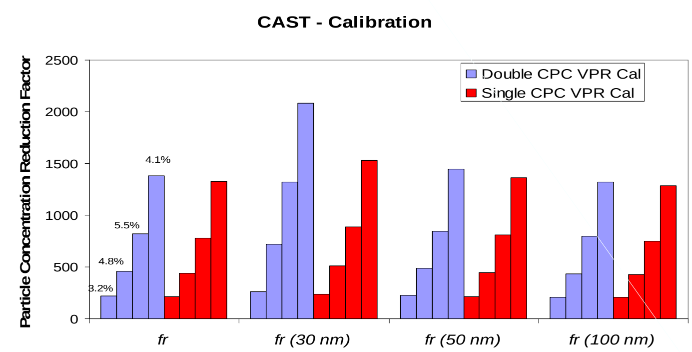

Figure 4: Calibration of the VPR with the single and the double CPC calibration method