Accuracy of Particle Number Counting systems (PNCS) influenced by different 23nm cutpoint calibration methods

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Introduction to PNCS

The Particle Measurement Program (PMP), organized under the Working Party on Pollution and Energy (GRPE) of the United Nations Economic Commission for Europe (UN/ECE), proposed a measurement protocol for particle number (PN) emissions from light duty vehicles (LDV). Additional the European Union (EU) has announced limits for particle number emission, scheduled for introducing from 2011 on. The PN counting system required in regulations consists of a Volatile Particle Remover (VPR), a hot dilution in front, and a cold dilution behind the Evaporation tube (300 – 400 °C). After the diluted aerosol passed the VPR it shall be passed to a Condensation Particle Counter (CPC).

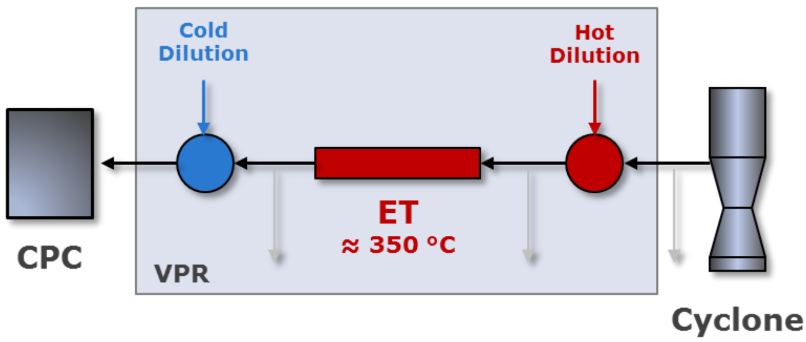

Figure 1: Basic design of a PMP-conform Particle Number Counting System.

Motivation: Improvement of PNCS accuracy

At present, there are many different PNCSs in Europe, used for research, development and certification purposes.

Compared to the very small error limits of gaseous analyzers, there is still room for improving the accuracy of PNCSs. Besides that, the accuracy of the PNCSs dilution system (durability, pressure stability) the CPC itself has a big impact on the total counting accuracy of the complete system.

Once we noticed from time to time, on first sight, unexplainable deviations between different identical counting systems with automotive exhaust, HORIBA started a long-term investigation to find out the reasons. Interestingly these deviations were strongly dependent on the exhaust type. High deviations occurred more often at gasoline direct injected (GDI) vehicles than at Diesel ones.

By measuring the particle size distribution (PSD) of different exhaust types with a "Fast Particulate Spectrometer" (like in our case the DMS 500 from Cambustion) it can be shown, that the emitted PSD changes significant from the well-known Diesel to GDI vehicles.

The regulation requires a CPC-counting-efficiency of 50 % for a particle size of 23 nm (electro-mobility-diameter) and larger than 90 % (against an electrometer) for a particle size of 41 nm. The linearity and a correction factor are normally calibrated at 55 nm.

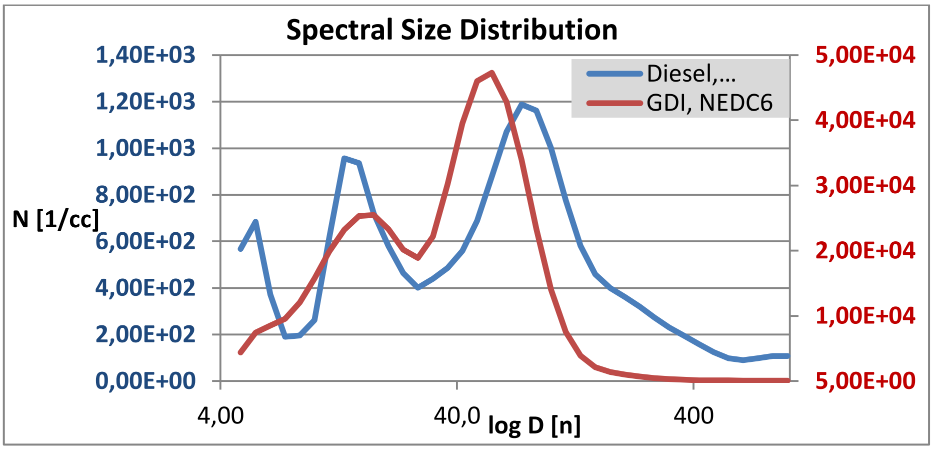

Figure 2: Measured particle size distribution by DMS 500; sampled from a full flow dilution tunnel, without a volatile particle remover; each averaged over a NEDC driving cycle.

This means that the CPC has a cutoff point – or “cutpoint” for particles smaller than 23 nm. This cutpoint was chosen not because smaller particles where not of interest (means considered to have health impacts). It was chosen because it turned out that decreasing the cutpoint of the CPC lead to bigger uncertainties of the detected particle numbers and the detection of “phantom particles”. One explanation for this effect is, that there might result re-condensed particles after the VPR, which should not be counted.

The graph in **Figure** 3 shows the same PSD as in **Figure** 2 but multiplied by the spectral detection efficiency curve of a standard, PMP-compliant CPC. The areas under the two graphs are equal to the total particle numbers, which were theoretically counted by a PNCS (neglecting the missing VPR). For these two typical particle size distributions of a Diesel and a GDI vehicle, it can be seen, that the GDI distribution has a bigger weighting to smaller particles than the Diesel distribution. Stated in numbers the Diesel particle number distribution from 0 to 40 nm gives only a share of 3 % (from 0-1000 nm). In case of the GDI distribution it is 13 %. In other words: If the CPC detection efficiency around its cutpoint (approximately up to 40 nm) differs from one PNCS to another, it causes an about 4 times higher influence to the total counted particle number at the GDI vehicle compared to the Diesel vehicle. The share of small particles up to 40 nm after a VPR could be even higher compared to the particle distributions we measured here: Particles with a solid core, but a volatile coating will shrink in the VPR, because they lose their volatile fractions.

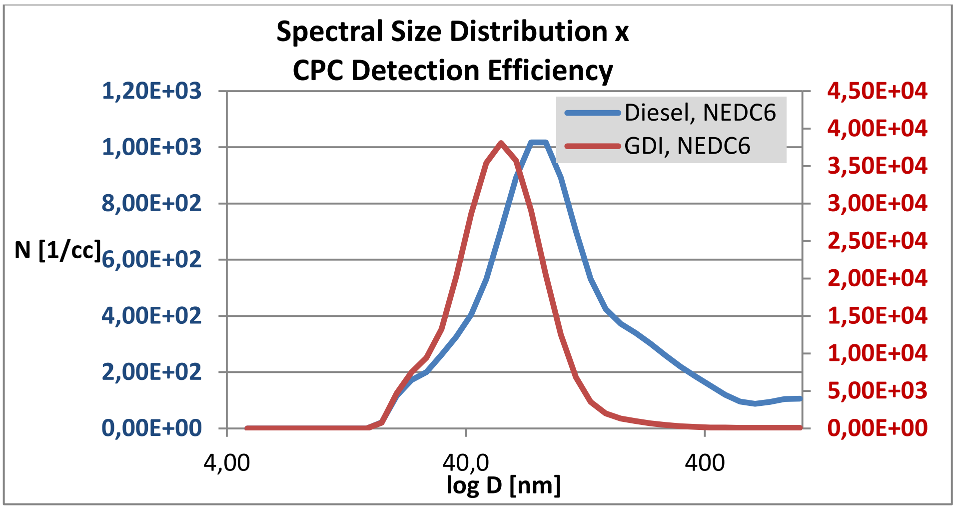

Figure 3: Measured particle size distribution by DMS 500 multiplied by the spectral detection efficiency curve of a standard, PMP compliant CPC; sampled from a full flow dilution tunnel, without a volatile particle remover; each averaged over a NEDC driving cycle.

CPC evaluation program

In order to monitor the CPC counting (detection) efficiency calibration, HORIBA developed a method which is based on a reference CPC and soot particles. With this method, more than 100 CPCs where evaluated under laboratory conditions.

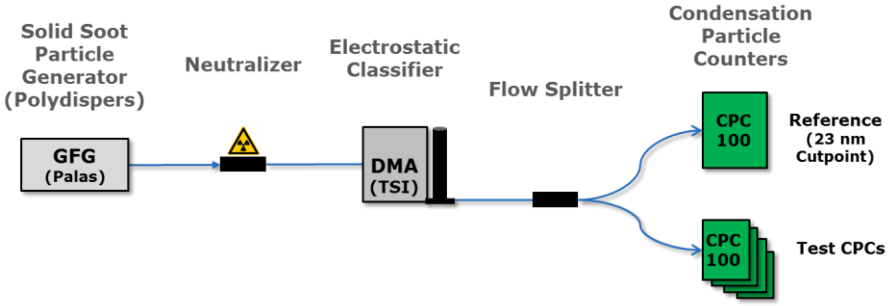

Figure 4: CPC evaluation setup.

The collected data reveal significant differences between 23 and 55 nm particles concerning deviations to the reference CPC.

It could be confirmed on some of these CPCs with a higher deviation, that these deviations are constant over the time – that means they are related to the calibration of each CPC.

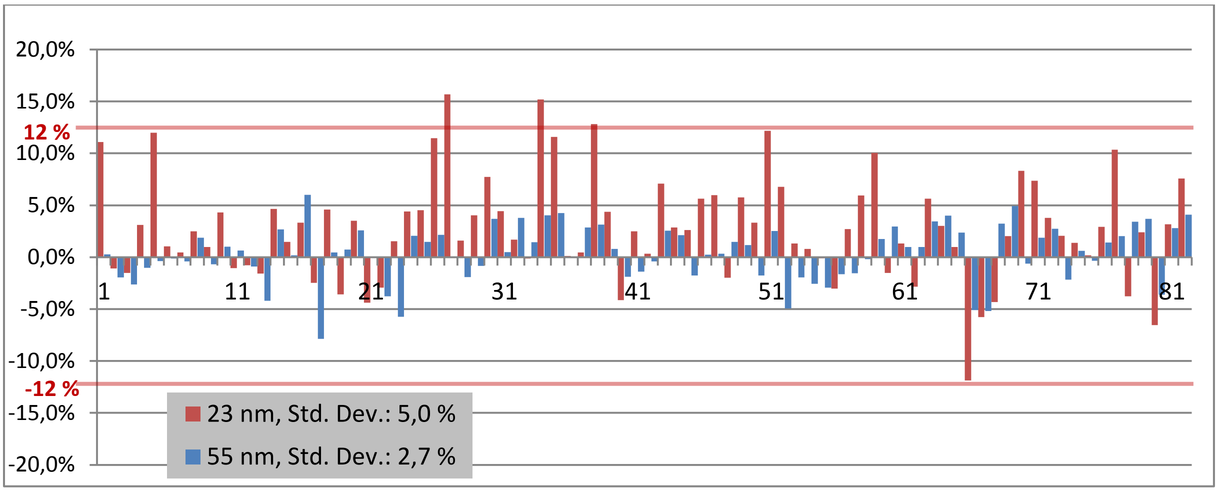

Figure 5: Measured deviations of counting efficiencies of 81 CPCs against one reference CPC at each 23 and 55 nm particle sizes. The reference CPC and all test CPC where calibrated in an external, certified calibration lab, PMP conform.

Different CPC Calibration Methods

There are two PMP compliant CPC calibration methods: The basic and standard method a) traces back to an electrometer as reference. Effectively for this method only Poly-Alpha-Olefin (PAO) particles, or those with similar high detection efficiencies, can be used. Method b) traces back to a reference CPC. This reference CPC must be calibrated by method a).

To understand better the characteristics of method a) it is necessary to know some facts about the electrometer (EM) in general:

- The EM defines the only traceable standard so far for the CPC calibration.
- In the calibration-range, the EM has a much worse accuracy, compared to a CPC. The minimum concentration per cm^3 is around 2000.

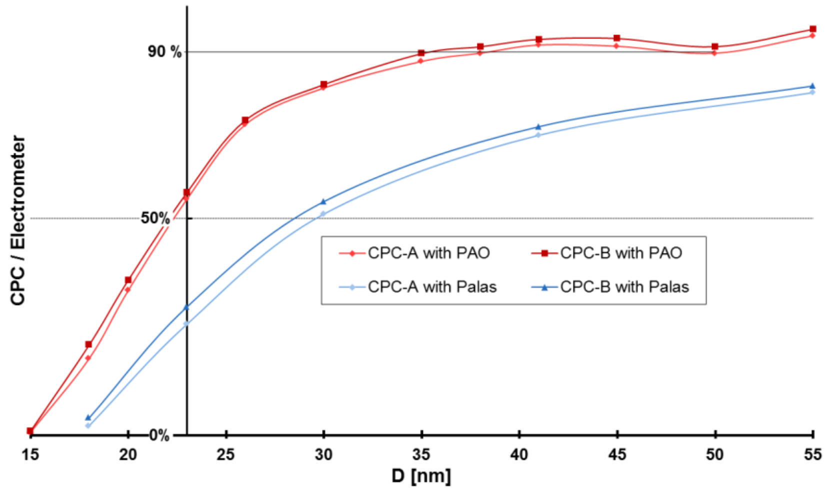

Figure 6: PMP-conform counting efficiency curves of a CPC for PAO (Poly-Alpha-Olefin) and Soot particles.

Conclusions

In how far do the two different CPC calibration methods influence the quality and stability of the counting efficiency curve?

The large amount of recorded comparative measurements between the 81 test CPCs and the one reference CPC (**Figure 5**) proves that the reference method b) in conjunction with soot particles is more sensitive at the 23 nm cutpoint than method a). But: This statement is only valid regarding this one reference CPC, provided that it has the same cutpoint as the test CPC, because the cutpoint of the reference CPC underlies the same uncertainty.

In other words: method b) is able to provide much higher calibration accuracy concerning the reference CPC as the standard. To reduce the uncertainty of the calibration level of the reference CPC, it is necessary to go one step further. It is recommended to calibrate the reference CPC (by method a)) with a significant smaller cutpoint than 23 nm – e.g. 10 nm. This has the effect that the reference CPC already operates on its counting-efficiency-plateau when calibrating the 23 nm cutpoint. This recommendation will also be written as a requirement in the upcoming ISO norm for CPC calibration.

The main reason for the worse accuracy regarding method a) might be related to the significant higher (86 % at 23 nm) counting efficiency of PAO particles compared to soot particles, as shown in Figure 6.

In Future Horiba Europe will offer to carry out the calibration by method b) with a 10 nm reference CPC, besides the standard method a) by an external institute.

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17th ETH Conference on Combustion Generated Nanoparticles

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Content

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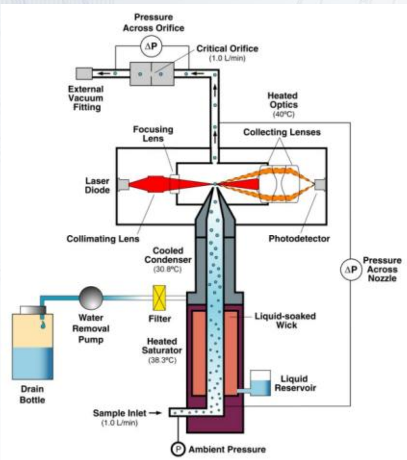
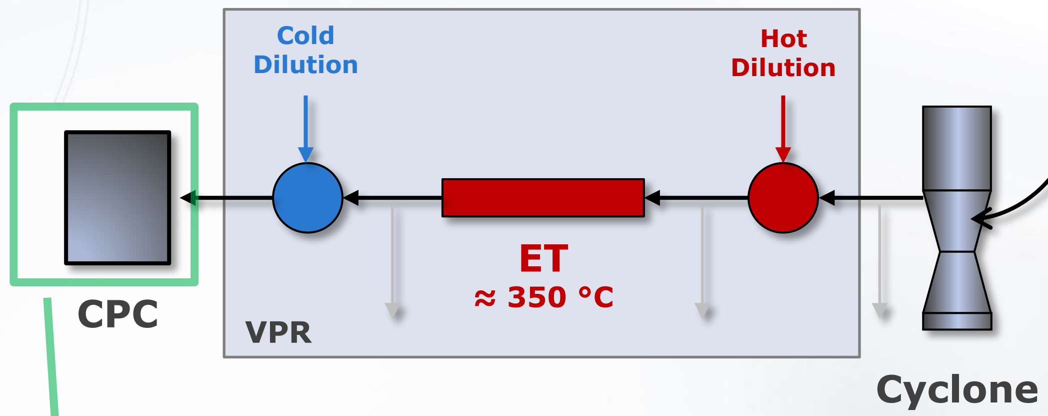
Automotive Test Systems

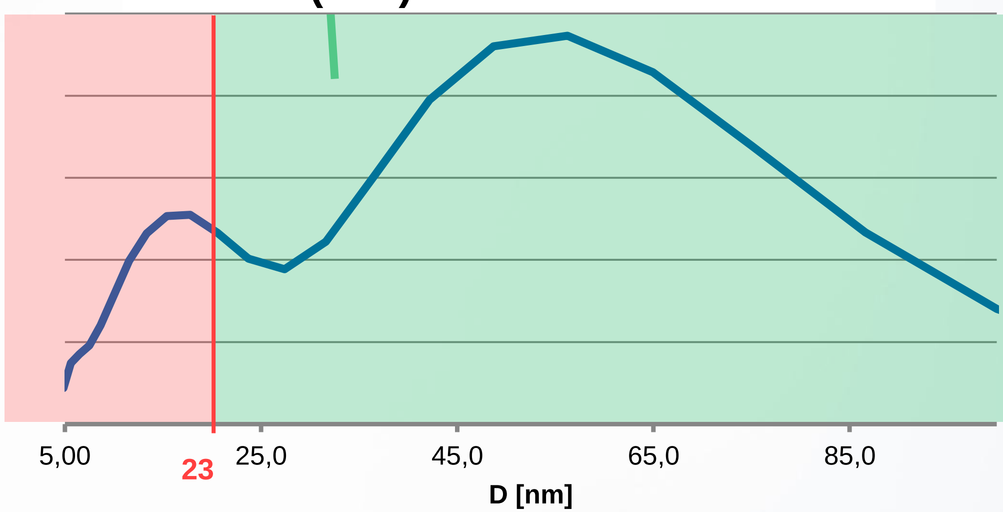
1) Introduction to PNCS

Basic Design of a PMP conform PNCS





Exhaust (GDI) Particle Size Distribution



2) Motivation: Improving PNCS accuracy

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- On customer site: Correlation-car tests (Diesel & GDI) with different PNCS
- This situation is possible:
  - Diesel: Very good correlation
  - GDI: > 25 % deviation between two identical PNCS
- What might be the reason?

2) Motivation: Improving PNCS accuracy

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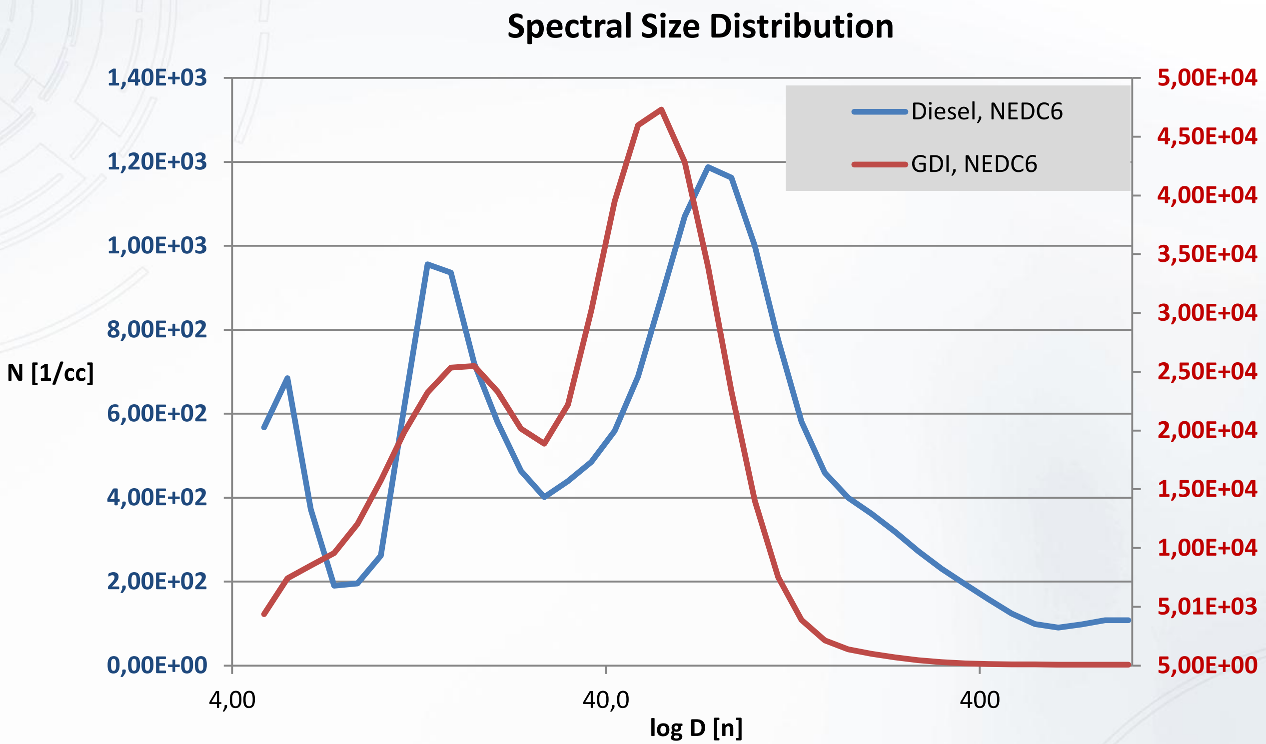
Particle Size Distributions



- Measured by DMS 500
- sampled from CVS, without a volatile particle remover; averaged over a NEDC driving cycle

2) Motivation: Improving PNCS accuracy

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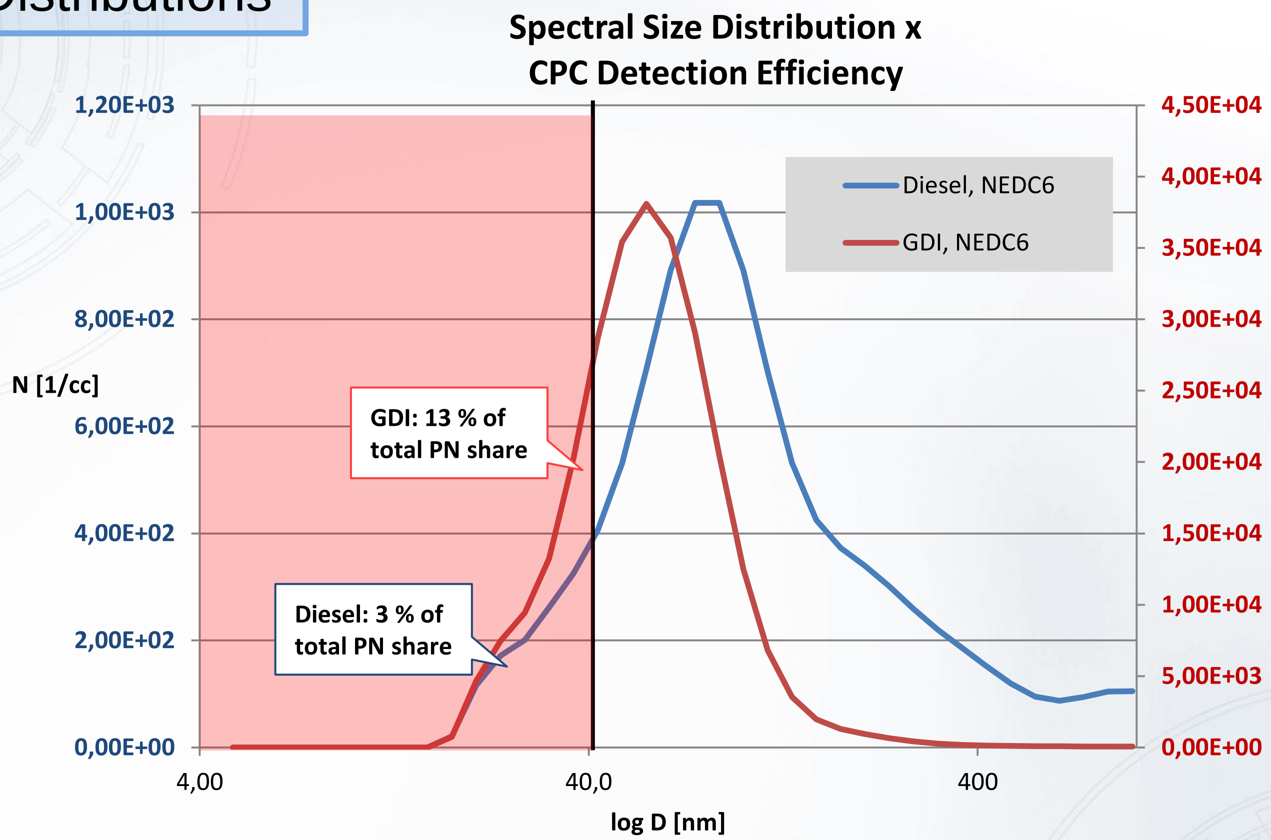
Particle Size Distributions



- Size distribution multiplied by the spectral detection efficiency curve of a standard, PMP-compliant CPC

3) Results of long term CPC evaluation

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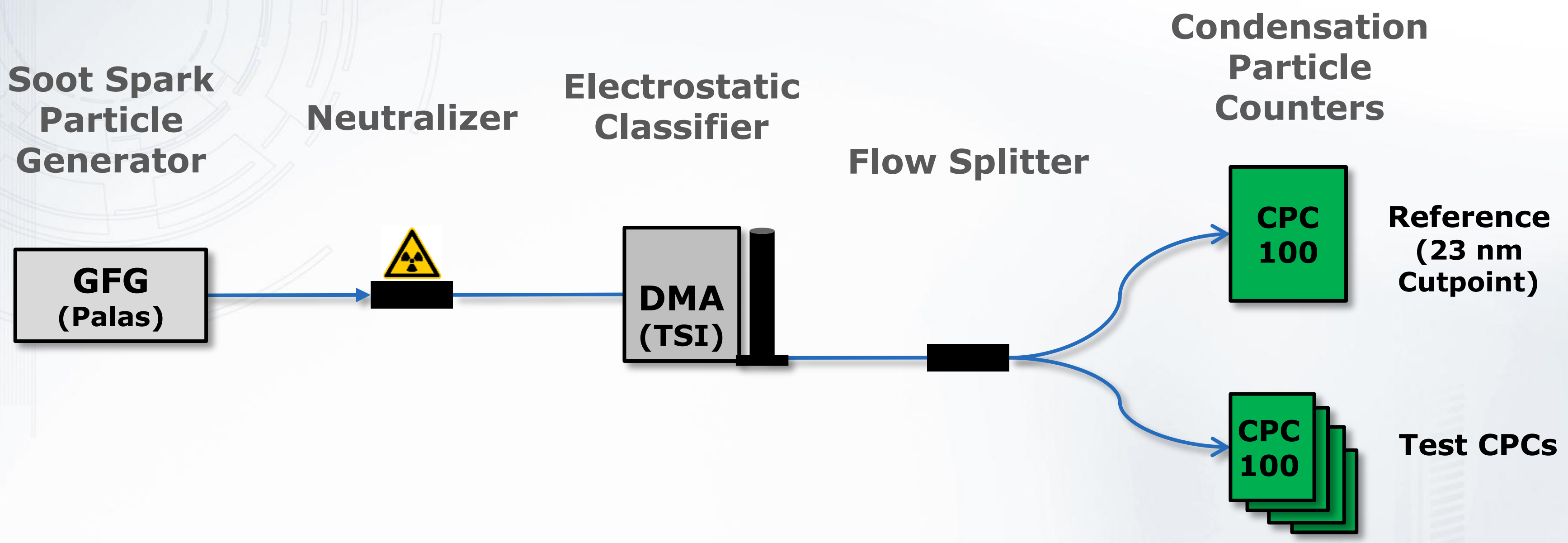
Lab Setup



The CPCs

- Have same counting efficiencies for any particles
- For any material there should be 0 % deviation between Ref. and Test CPCs

Particle Material

- To test CPCs withparticles most similar to exhaust, we choose thermally stable soot particles

3) Results of long term CPC evaluation

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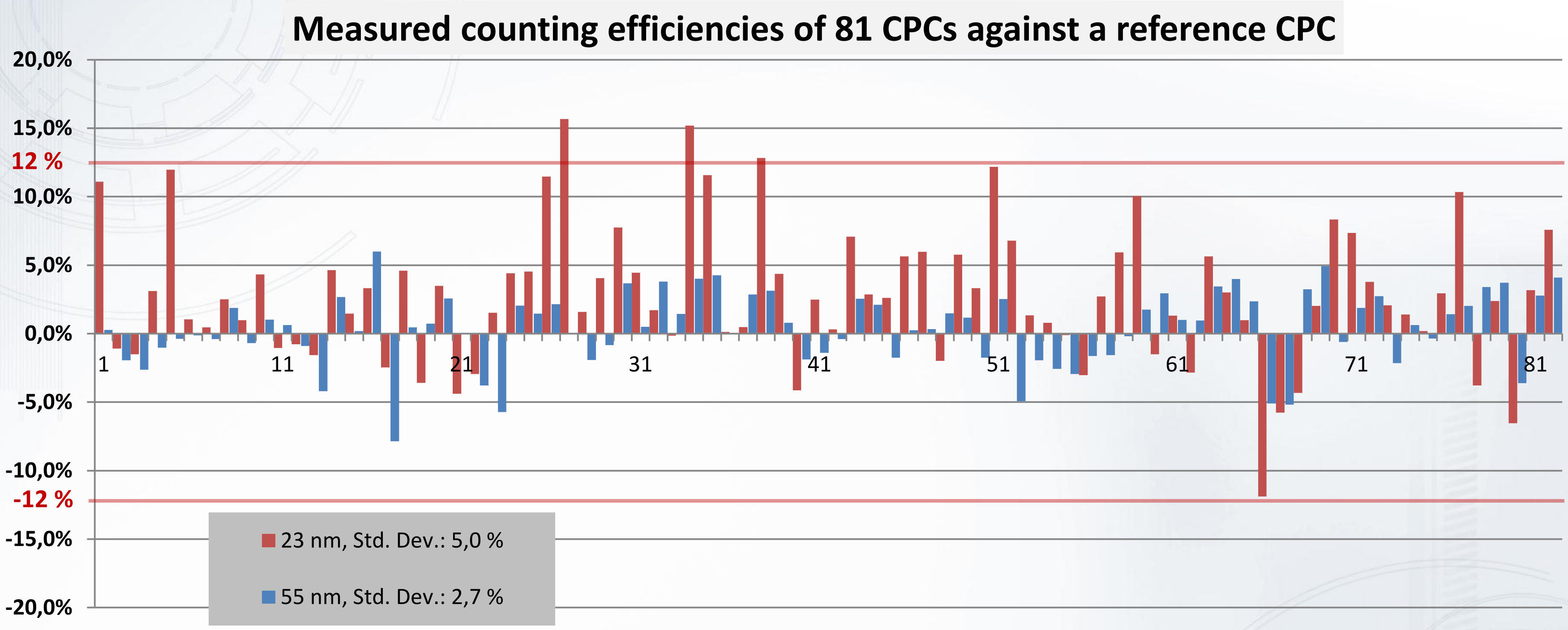
Results



The CPCs

- Where just calibrated by a certified calibration lab, by the "**Electrometer Method**"
- Are all PMP conform and within (50±12) % at 23 nm

4) The two CPC calibration methods

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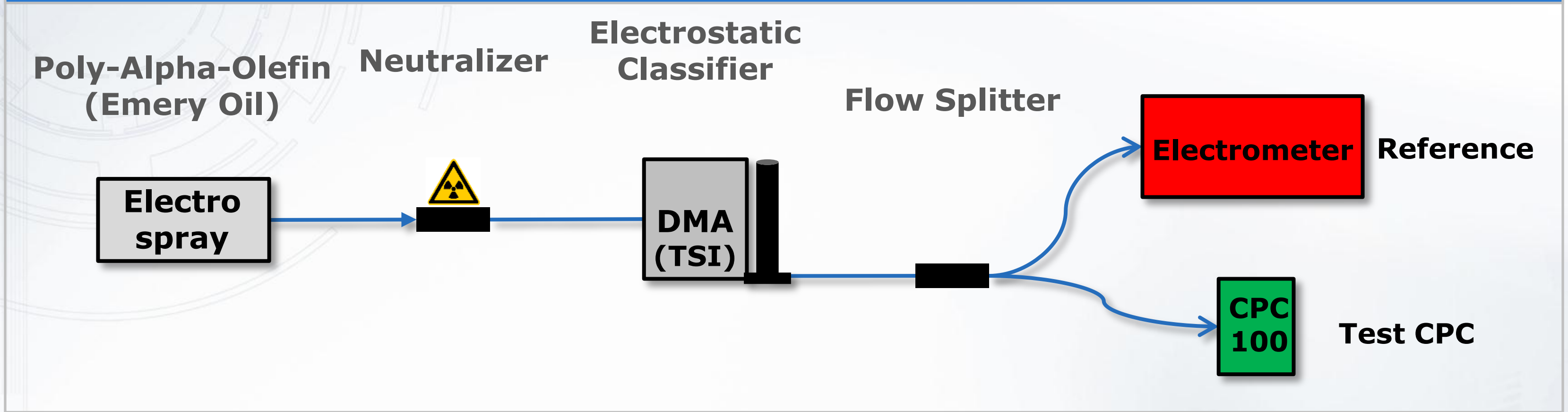
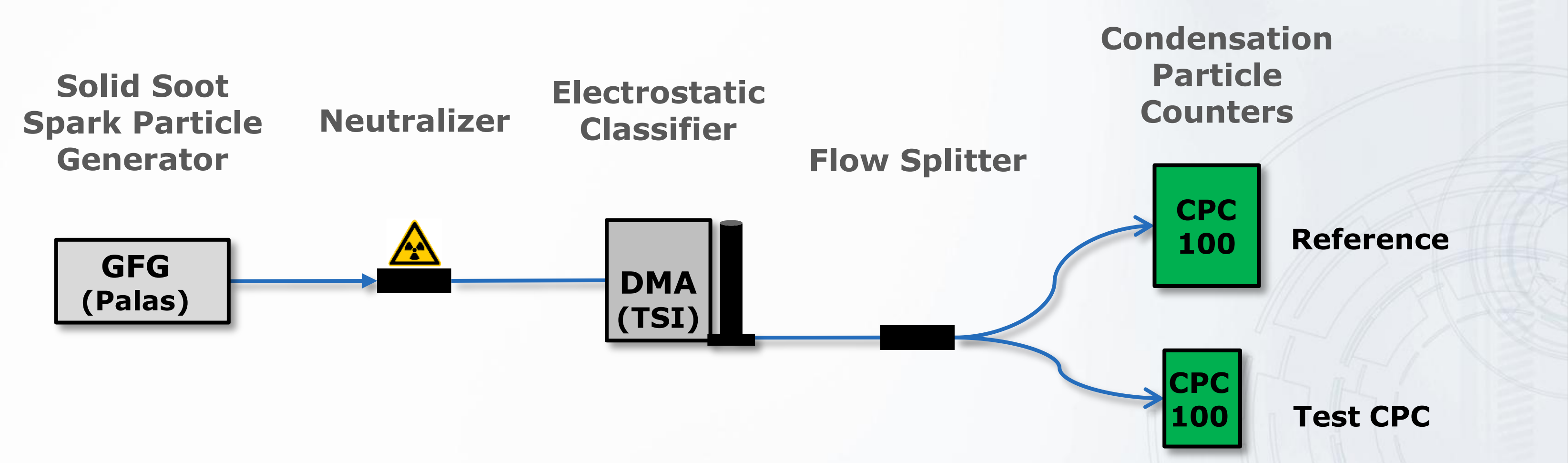
Method a) "Electrometer Method"



Method b) "Reference CPC Method"



4) The two CPC calibration methods

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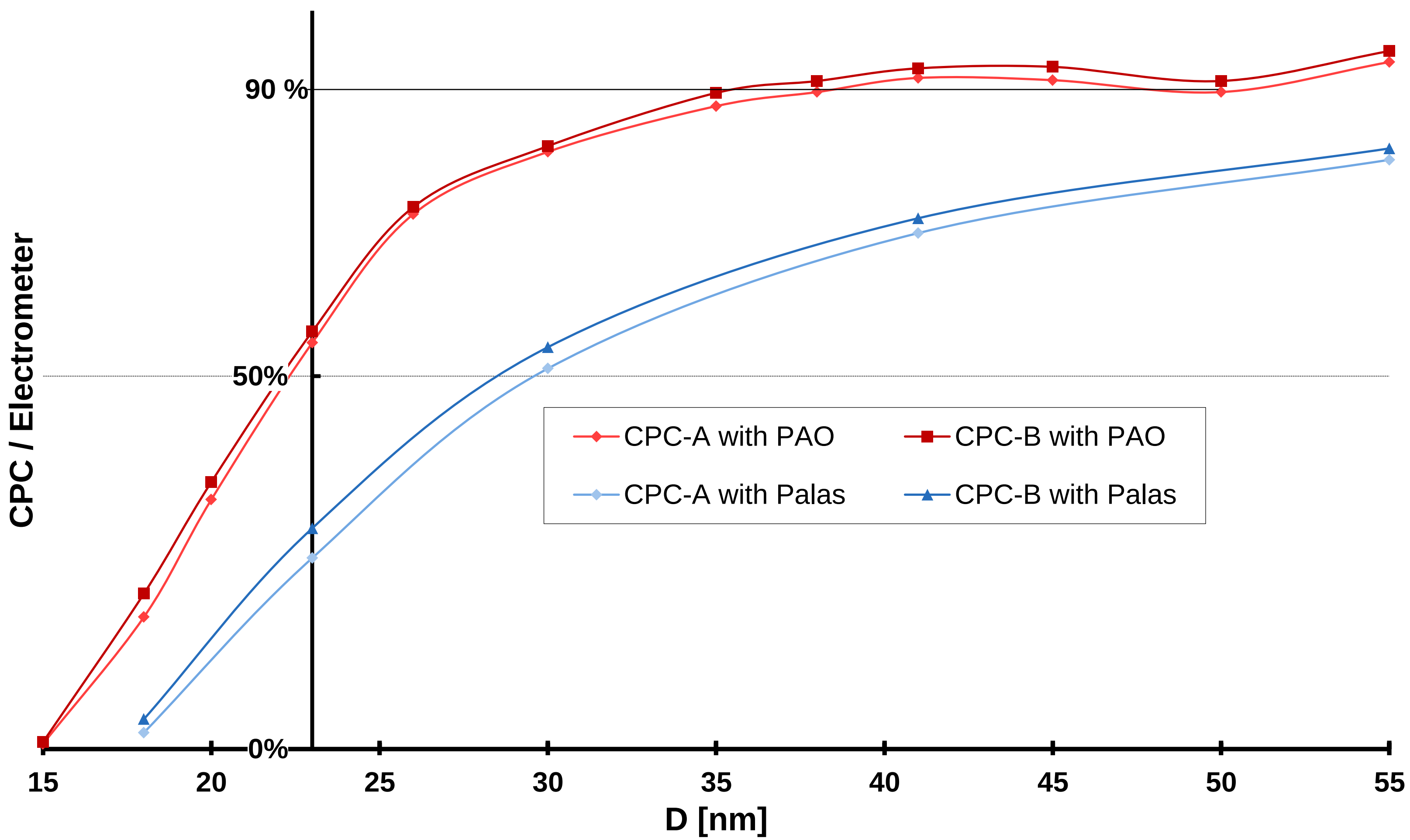
Different Particle Counting Efficiencies



4) The two CPC calibration methods

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Method a) “Electrometer Method”

- The EM defines the only traceable standard so far for the CPCs calibration.
- In the CPC calibration-range: EM has higher uncertainty compared to a CPC.
- Minimum concentration is c ≈ 2000 / cm^3
- Effectevely only PAO particles (or similar counting eff.) can be used
  - **≈ +86 % higher counting eff. than soot particles at cutpoint!**

Method b) “Reference CPC Method”

- PMP conform (Reference CPC must be calibrated by Method a))
- Technical easier to handle
- CPC-Evaluation program proved higher accuracy, in particular at cutpoint
  - High accuracy at “COPIES” of reference CPC
- How to stop inheritance of cutpoint uncertainty for the reference CPC?
  - Cross-checking Ref. CPC with other CPCs, or
  - **Change cutpoint at ref. CPC to 10 nm! (New ISO)**

5) Conclusions

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- The reference CPC method has the potential to achieve a higher calibration stability and repeatability
- Further investigations concerning different calibration materials and the two methods should be carried out
- We need to go ahead to reach a higher PNCS accuracy
- HORIBA Europe will provide ref. CPC method, with 10 nm Cutpoint

Do you have any questions?