

On-Site Checks of the Particle Number Measurement Systems with Polydisperse Aerosol

Barouch Giechaskiel and Alexander Bergmann
AVL List GmbH, Austria

ABSTRACT

Since 2011 a particle number (PN) limit was introduced in the European light-duty diesel vehicles legislation. The PN measurement systems consist of i) a hot diluter and an evaporation tube at 300-400°C for the removal of the volatiles (Volatile Particle Remover, VPR) and ii) a particle number counter (PNC) with a 50% cut-point (cut-off) at 23 nm. The PN measurement systems are calibrated and validated annually with monodisperse aerosol: The VPR for the particle concentration reduction factor (*PCRF*) and the PNC for the linearity and the cut-off size. However, there are concerns that the PN measurement systems can drift significantly over this period of time, raising concerns regarding the validity of the previous measurements, especially if the yearly validation fails.

In this paper we describe some relatively fast and simple on-site checks for the evaluation of the proper operation of the PN measurement systems with polydisperse aerosol, thus avoiding the need of electrostatic classifiers and radioactive sources. The necessary equipment are i) a particle generator that produces polydisperse aerosol with thermally stable particles of known count median diameter (CMD) at different concentrations and ii) a calibrated reference PNC with a nominal 50% cut-point at 23 nm and linear response at the whole measurement range.

The recommended checks for the PNC under evaluation (test PNC) are: 1) *Linearity check*: The test PNC measures in parallel with the reference PNC polydisperse aerosol with CMD >50 nm at different concentrations. The differences, similarly with the legislation requirements, have to be within 10%. 2) *Cut-off size check*: Only the test PNC measures polydisperse aerosol with CMD=10 nm. The concentration measured by the test PNC should be <100 p/cm³. If a PNC with a 50% cut-point at 10 nm or lower is available another possibility is to produce an aerosol with CMD=23 nm and compare the ratio of the test PNC to the reference PNC, which should be within the legislation requirements (0.38-0.62).

The recommended checks for the VPR are: 3) *PCRF check of the VPR*: The reference PNC measures upstream and downstream of the VPR (set to a low *PCRF* <1000) thermally stable aerosol with CMD around 50 nm. Similarly with the legislation requirements, the upstream to downstream ratio has to be within 10% of the *PCRF* setting. 4) *Relative check of the rest PCRFs*: The reference PNC measures downstream of the VPR and different *PCRFs* are measured. The *PCRF* corrected emissions for each *PCRF* measured should be within 10% of the previously checked low *PCRF*.

Theoretical calculations showed that these checks can identify a drift of the VPR or PNC and experimental data confirmed that they work in practice.

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INTRODUCTION

The particle number (PN) measurement was introduced in the Euro 5b light duty diesel vehicle emissions regulation with a limit of 6×10^{11} p/km after the work of the Particle Measurement Program (PMP) group [1, 2]. Euro 6 legislation will require measurements from spark ignition vehicles as well. Euro VI for heavy-duty engines will also introduce a PN limit [3, 4]. Thus, most of the automotive laboratories,

test cells and chassis dynamometer rooms have been equipped with PN measurement systems.

The PN measurement systems consists of two main parts: The sample pre-conditioning unit or volatile particle remover (VPR) and the particle number counter (PNC). The VPR initially dilutes the sample at least 10 times at a temperature of 150°C. The diluted sample then passes through an evaporation tube with wall temperature between 300 and 400°C and then is further diluted in a secondary diluter at ambient temperature. The dilutions (more specifically particle

concentration reduction factors, *PCRFS*, see main text) of the VPR are calibrated with monodisperse particles of 30, 50 and 100 nm. The losses of the VPR are restricted by the legislation, with the requirement that the *PCRFS* ratios of 30 and 50 nm are <1.3 and <1.2 times the *PCRFS* at 100 nm respectively. The diluted and thermally pre-treated sample is then measured with a PNC which has counting efficiencies at 23 nm and 41 nm of 0.50 ± 0.12 and >0.90 respectively. The 23 nm cut-off size was selected in order to exclude possible confounding of measurements by low volatility hydrocarbons present as nucleation mode particles, while including the primary soot (spherule) size of ~ 20 nm.

Legislation requires the execution of some checks before the beginning of a test, such as the zero checks of the PNC and the VPR, and the high response check of the PNC. However these checks cannot ensure that the system measures accurately because no comparison with a particle number concentration standard is conducted. Regarding the accuracy of the systems, legislation requires annual *calibration* or *validation* (yearly check that the system is within 10% of the calibration values). The yearly calibration or validation is not enough and doesn't ensure that all previous measurements were conducted correctly. If a validation fails (i.e. there is >10% difference to the calibration, e.g. due to a drift) after one year, the back-correction of the results is not always possible. The reason is that in many cases it is not known whether the drift happened gradually or whether it happened at one specific measurement. Moreover, in the second case it's not always possible to identify at which measurement it happened.

Drifts have been observed for both PNCs and VPRs. For example, PNCs seem to drift 5-10% every 3-6 months when measuring engine exhaust aerosol. The assumption is that gaseous compounds from the exhaust aerosol react with butanol to form esters that deposit on the saturators of the PNC, affecting the supersaturation profile and consequently the cut-off size [5]. Other possible reasons include the degradation of the working fluid (butanol) itself or even accumulation of humidity in the butanol tanks. VPRs can also drift due to the drift of the parts they contain (e.g. temperature and pressure sensors, mass flow controllers etc.), contamination (e.g. orifices contamination [6]) or small leaks that become significant at high dilutions. Thus, it is important for the everyday users to find ways of checking their instrumentation; checks that ensure the accurate operation of the systems.

For other test beds equipment (e.g. gas analyzers) there are calibration procedures that are conducted daily, giving confidence to the users that the equipment operate correctly. The difficulty for the PN systems is that there is no PN standard that can be used for daily calibration. The calibrations, according to the procedures described in the legislation (for the VPR and PNC), are time consuming and need a big investment in equipment. Moreover, a radioactive source is necessary making it difficult, if not impossible for some countries, because special handling and operation is

required. Finally, the calibration procedure itself is not so simple and it needs specialized personnel. Some simpler checks for the VPR that were mentioned in [7, 8] are the gas check and the check with polydisperse aerosol. Beginning with the polydisperse check with a Scanning Mobility Particle Sizer (SMPS) [9], it is relatively easy and fast to perform: A SMPS measures the size distribution upstream and downstream of the VPR system and the upstream to downstream ratio is compared to the (*PCRFS*) setting of the instrument. One basic precondition is the purchase of a SMPS which includes a radioactive source. In addition the operation of the SMPS is not very simple. The other check, the gas check, uses a gas with known concentration at the inlet of the VPR and the diluted concentration is measured at the outlet of the VPR with a gas analyzer. Then the gas dilution ratio is compared with the *PCRFS* setting of the VPR. The gas check was found to be the easiest and fastest in practice, but the results are not always meaningful or comparable because the *PCRFS* of the VPRs includes the particle losses. Thus, a gas check of the dilution is not directly comparable with the VPR setting and doesn't confirm that the loss mechanisms inside the VPR have remained the same. However, it is still a very good check for identifying leaks in the VPR. Regarding the PNC, a simple check of its linearity is with polydisperse aerosol and another PNC. The method was followed in the light-duty PMP inter-laboratory exercise, and was found to be very useful [10].

In this paper we recommend some checks that don't require special investment in equipment and they are simple and fast to execute. It is also possible to conduct them on-site, thus avoiding the need to remove the PN system from its sampling location. Initially the requirements for the reference equipment will be presented and then the checks for the PNC and for the VPR will be described.

REFERENCE EQUIPMENT

The only required equipment for the recommended checks are a particle generator and a reference PNC.

PARTICLE GENERATOR

Particle generators that are typically used include:

- Evaporation condensation aerosol generators [11] for metal particles like Ag, Au and salt particles like NaCl
- Spray atomizer generators for solutions and dispersions [12]
- Electrospray aerosol generators for Emery oil (poly-alpha-olefin, PAO) droplets, or sucrose particles [13]
- Spark discharge between particle delivering electrodes generators for metal, metal oxide or carbon particles [14]
- Diffusion flame aerosol generator for soot particles [15]

The only requirement in legislation regarding the VPR calibration is that a thermally stable aerosol should be used, in order to avoid evaporation of particles inside the VPR. Regarding PNCs the generation method is not specified, but

the particles should be PAO (Emery oil) or flame soot particles (CAST). Effect of the material on the calibration results has been observed for both VPRs and PNCs [8, 16, 17]. The target of the paper is not to examine the effect of the material on the results, but the suitability of the recommended checks for the evaluation of the PN systems. For this reason, all tests (calibration, validations and recommended checks) were conducted using the same generation method/material. The generator that was used here was a diffusion flame generator (mini CAST) followed by hot dilution and thermal pre-treatment in order to ensure thermally stable aerosol. Details will be given in the text for each experimental set up. The reason that this generator was chosen was that it was available, easy to operate, well characterized (size distributions) and could be used for both PNC and VPR calibration. We expect that the experimental results of this work would be similar with other generation principles and materials.

However the theoretical evaluations that will be presented are based on the assumption that the generated distribution is known (i.e. the geometric mean diameter and the geometric standard deviation of the distribution). The concentration is not important since the checks are relative, but in many cases the concentration has to be adjusted at specific levels, so a diluter is necessary as well. The effect of the different size distributions on the results will be discussed later in the text. However, if the size distribution is not known or the uncertainty is very high, then the results of the checks could lead to wrong conclusions. For example, a check could show that the VPR or test PNC failed, but in reality it could be that the size distribution was not in the right range.

REFERENCE PARTICLE NUMBER COUNTER (PNC)

The reference PNC (PNC_{Ref}) that will be used for the check must have a valid calibration certificate (for the absolute concentrations) that also confirms its linear response at the whole measurement range (i.e. the differences to the original reference instrument should remain the same at different concentrations). In the market, at the moment, only the PNCs with 50% cut-point of 23 nm ($d_{50\%} \approx 23$ nm) are delivered with linearity certificates. This means that any other PNC has to be checked for its linearity at the range that will be used (e.g. by comparing with a $d_{50\%} \approx 23$ nm PNC or an electrometer). In order to avoid this check we recommend using a PNC_{Ref} with $d_{50\%} \approx 23$ nm. The suitability of the PNCs with different $d_{50\%}$ as reference instruments will also be discussed in the main text. It is also assumed that the reference PNC and the test PNC are always corrected for their slope factor, the pressure and temperature conditions at their inlet and they are normalized to the same temperature and pressure conditions [18].

PARTICLE NUMBER COUNTER (PNC)

In this section the PNC of the PN system will be examined. Initially, the calibration and validation procedures required in the legislation will be described. Then, our recommended checks will be mentioned. A theoretical approach will follow and finally some comparisons with experimental data will be given.

CALIBRATION

According to the legislation [1] a calibration certificate for the (test) PNC demonstrating compliance with a traceable standard within a 12 month period prior to the emissions test or after any major maintenance has to exist. Calibration shall be traceable to a standard calibration method:

- By comparison of the response of the PNC under calibration (PNC_{Test}) with that of a calibrated aerosol electrometer when simultaneously sampling electrostatically classified calibration particles. In this case, calibration shall be undertaken using at least six standard concentrations spaced as uniformly as possible across the PNC's measurement range.
- By comparison of the response of the PNC under calibration with that of a second PNC (PNC_{Ref}), which has been directly calibrated by the above method. In the reference PNC case, calibration shall be undertaken using at least six standard concentrations across the PNC's measurement range. At least 3 points shall be at concentrations below 1000 p/cm^3 , the remaining concentrations shall be linearly spaced between 1000 p/cm^3 and the maximum of the PNC's range in single particle count mode.

In both cases the points will include a nominal zero concentration point produced by attaching HEPA filters of at least class H13 of EN 1822:1998 to the inlet of each instrument. With no calibration factor applied to the PNC under calibration, measured concentrations shall be within ± 10 per cent of the standard concentration for each concentration, with the exception of the zero point, otherwise the PNC under calibration shall be rejected. The gradient from a linear regression of the two data sets shall be calculated and recorded. A calibration factor equal to the reciprocal of the gradient shall be applied to the PNC under calibration. Linearity of response is calculated as the square of the Pearson product moment correlation coefficient (R^2) of the two data sets and shall be equal to or greater than 0.97. In calculating both the gradient and R^2 the linear regression shall be forced through the origin (zero concentration on both instruments).

Calibration includes in addition a check on the PNC's counting efficiency with particles of 23 and 41 nm electrical mobility diameters. The counting efficiencies of the 23 and 41 nm have to be 0.38-0.62 and >0.90 respectively.

A typical experimental setup can be seen in Figure 1 [16]. For our experiments a mini CAST generator was used to generate soot particles in a diffusion flame using propane as fuel [15]. The particles passed through an aerosol conditioner, where they were diluted with hot dilution air ($>150^{\circ}\text{C}$) and were heated in an evaporation tube with wall temperature of 350°C . A secondary cold dilution reduced the diluted sample temperature to ambient levels. Legislation doesn't require any thermal pre-treatment of the calibration (or validation) aerosol. However, we recommend the thermal pre-treatment of the aerosol, in order to mimic the non-volatile particles that are measured by the (automotive) test PNCs inside the PN measurement systems. The concentration of the aerosol was controlled by a dilution bridge. The dilution bridge initially splits the sample to two lines: One line has a throttling valve and the other line has a filter. Then the two lines are reconnected; by adjusting the throttling valve different concentrations can be achieved. The polydisperse aerosol was classified to an appropriate size in a differential mobility analyzer (DMA). The PNC under calibration (PNC_{Test}) and the reference PNC (PNC_{Ref}) were measuring downstream of the electrostatic classifier in parallel. Make up air flow was needed to equalize the flow, and a mixing orifice or chamber to ensure well mixing of the sample with the air and thus homogeneously mixed aerosol to the instruments.

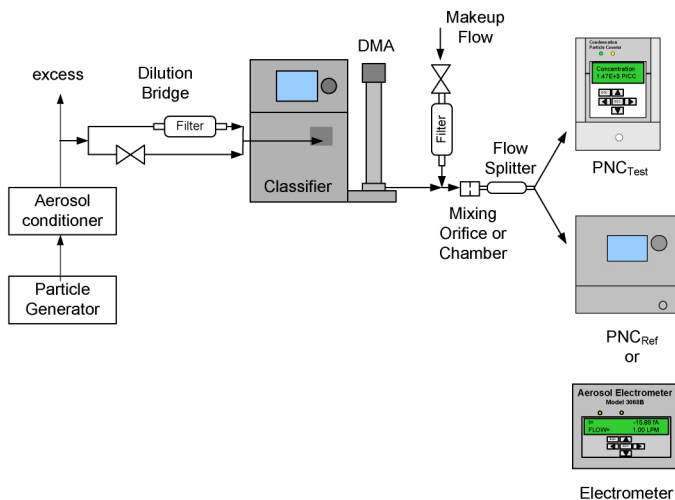


Figure 1. Example of an experimental setup for the calibration of a PNC.

VALIDATION

The same setup and tests are required with the exception of the 41 nm point which is not necessary to be checked. The same setup as in Figure 1 has to be used (i.e. monodisperse aerosol).

RECOMMENDED CHECKS

The recommended checks of the proper operation of the test PNC (PNC_{Test}) are the following checks with polydisperse aerosol:

- Linearity check using a reference PNC (PNC_{Ref}) with 50% cut-point at 23 nm and producing a polydisperse distribution with count median diameter (CMD) >50 nm.
- Cut-off size check without using any PNC_{Ref} and producing a polydisperse distribution with $\text{CMD}=10$ nm or
- Cut-off size check with a PNC_{Ref} with 50% cut-point at 10 nm or lower and producing a polydisperse distribution with $\text{CMD}=23$ nm.

Initially, the experimental setup of the recommended tests will be described. Then the theoretical background of these tests will be given and finally the theoretical calculations will be compared with experimental results.

Experimental

The experimental setup for the recommended checks can be seen in Figure 2. The setup is similar to the monodisperse calibration without the DMA. This means that a particle generator (with or without thermal pre-treatment) is necessary and a diluter for the adjustment of the concentration to the PNCs. Then the PNC_{Test} and PNC_{Ref} have to measure in parallel from a Y splitter using conductive tubes of equal lengths.

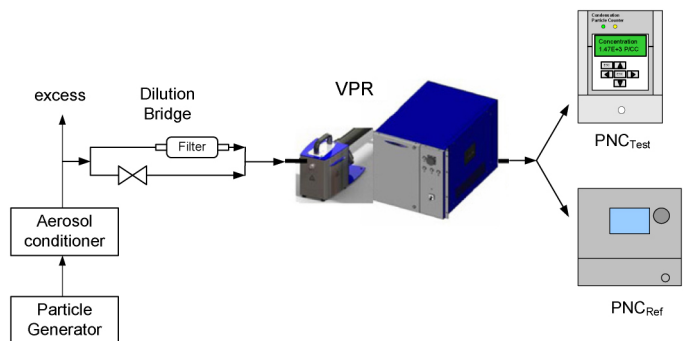


Figure 2. Example of an experimental setup for the recommended polydisperse check of a PNC_{Test} .

Our tests were conducted with a mini CAST [15] generator with thermal pretreatment in an APC [8] that served as a diluter as well. The reason that we used the APC was that the PNC_{Test} was inside the APC. Thus, it was simpler to leave it inside the instrument than removing it and conducting the measurements. As mentioned previously, the recommended checks should be easy and fast to conduct. The PNC_{Ref} for the linearity checks was a PNC with $d_{50\%}\approx 23$ nm. For the cut-off size checks we used a PNC_{Ref} with $d_{50\%}\approx 5$ nm. As mentioned in the Section 'Reference Equipment', similar instrumentation (Generator, pre-treatment, DMA, PNC_{Test} and PNC_{Ref}) was used for both the polydisperse and monodisperse aerosol tests (i.e. for the calibration, see Figure 1). The reason is that target of these tests was to compare the results of the recommended tests with the results of the

calibration method, so any effect of different calibration material or instrumentation should be minimum.

Theoretical Investigation

In order to cover all possible (and extreme) ranges of PNCs with $d_{50\%} \approx 23$ nm the following three cases were considered:

- A: a typical medium case
- B: a smooth curve
- C: a steep curve

All three cases are within legislation requirements as [Table 1](#) shows. The counting efficiency curves are shown in [Figure 3](#).

Table 1. Characteristic parameters of three legislation compliant PNCs (counting efficiencies at 23 nm 41 nm and slope at a large size).

PNC case	A (typical)	B (smooth)	C (steep)
23 nm	0.50	0.38	0.61
41 nm	0.90	0.90	0.90
Slope	1.00	1.10	0.90

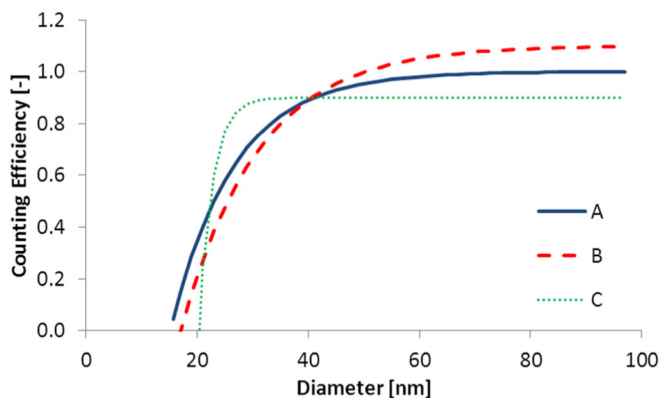


Figure 3. Three PNC counting efficiency curves compliant to the legislation (see [Table 1](#)).

After correcting with the slope (as required by the legislation) the counting efficiencies are as shown in [Table 2](#). Note that the slope goes to 1 but the 23 and 41 nm counting efficiencies are outside the original legislation requirements. Although the intention of the legislation was to have the counting efficiencies within the requirements even after correcting for the slope, the way that is written in the text doesn't exclude the cases presented here. Thus, these cases that will be examined cover almost all legislation compliant PNCs, but basically only case A is the most typical. For all theoretical evaluations the PNCs were assumed to have the counting efficiencies presented in [Table 2](#) (i.e. they were corrected for the slope). All three cases (A, B, C) are considered to have a 50% cut-point at approximately 23 nm ($d_{50\%} \approx 23$ nm) and whenever that a PNC with $d_{50\%} \approx 23$ nm

was used all three cases were considered (unless otherwise specified). The specific PNCs are sometimes called PMP PNCs.

Table 2. Characteristic parameters (counting efficiencies at 23 and 41 nm and slope at a large size) of three legislation compliant PNCs $d_{50\%} \approx 23$ nm after correcting for the slope.

PNC case	A (typical)	B (smooth)	C (steep)
23 nm	0.50	0.67	0.59
41 nm	0.82	1.00	0.97
Slope	1.00	1.00	1.00

Similarly we considered some extreme cases for PNCs with 50% cut-points of around 10 nm and 3 nm, which after correction with the slope they become as [Figure 4](#) shows. These PNCs are named as PNCs with $d_{50\%} \approx 10$ nm or $d_{50\%} \approx 3$ nm. The PNCs with $d_{50\%} \approx 23$ nm are also included in [Figure 4](#).

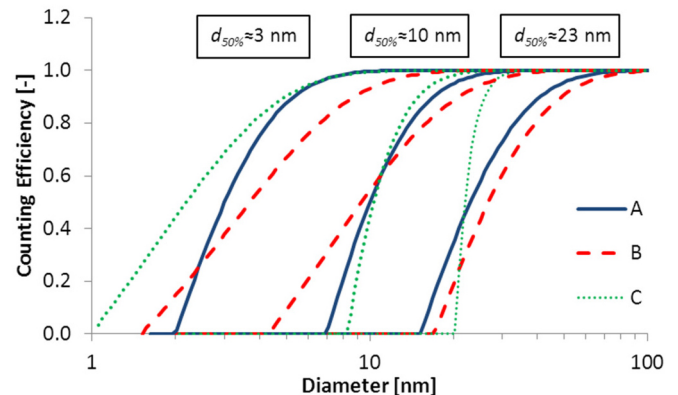


Figure 4. Counting efficiency curves of PNCs with different 50% cut-points. A, B, C refer to PNCs with a typical, a smooth or a steep counting efficiency curve respectively.

At a next step we considered polydisperse aerosol of various log normal distributions. In a lognormal distribution the arithmetic mean can be calculated by using the logarithm of the diameters, defined as the geometric mean diameter. For the count (number) distribution, the geometric mean diameter is customarily replaced by the count median diameter (CMD), the diameter for which one half the total number of particles are smaller and one-half are larger. For the lognormal distribution geometric mean diameter and CMD are equal. We considered CMDs from 10 nm up to 100 nm with different geometric standard deviations (σ), typical for the specific medians ([Table 3](#)). These ranges should cover most of the cases typically encountered in real life or that can be produced by the existing particle generators. Different standard deviation would slightly affect the results but they were not examined in detail because it is difficult to encounter in real life; however their effect on the results will