

Calibration and Validation of Various Commercial Particle Number Measurement Systems

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ABSTRACT

Measurement of particle number was introduced in the Euro 5/6 light duty vehicle emissions regulation. Although particle number measurement systems have to be calibrated by the manufacturers, labs have to validate the proper operation of their systems within one year of the emissions test. The systems must achieve a >99% reduction of an aerosol containing 30 nm tetracontane ($\text{CH}_3(\text{CH}_2)_{38}\text{CH}_3$) particles (C40) with an inlet concentration $>10^4 \text{ \#/cm}^3$. They must also include an initial heated dilution stage with dilution of at least 10 which outputs a diluted sample at a temperature of 150°C-400°C. The system as a whole must achieve a particle number concentration reduction factor for particles of 30 nm and 50 nm electrical mobility diameters, that is no more than 30% and 20% respectively higher, and no more than 5% lower than that for particles of 100 nm.

In this paper the terms dilution factor, penetration, losses, particle number concentration reduction factor and volatile removal efficiency are defined. Then, various commercial instruments, like the Solid Particle Counter (SPCS) from Horiba, the NanoMet-C from Matter Eng., the ejector diluter and the thermodenuder from Dekati are characterized. The penetrations, the particle number concentration reduction factors and the volatile removal efficiency of the above systems are discussed and compared with the legislation requirements. Finally, some calibration/validation issues are discussed, like the effect of the under-

pressure downstream of the electrostatic classifier and the use of one or two particle number counters for the calibration. The importance of a stable at high temperatures aerosol is also pointed out.

It is also shown that the systems can be checked using polydisperse aerosol but still many parameters need to be considered (e.g. concentration range, pressure upstream and downstream of the systems). Till more experience is gained, labs are highly recommended to use simple gas dilution factors to check their systems.

INTRODUCTION

The particle number was introduced in the Euro 5/6 light duty vehicle emissions regulation with a limit of $6 \times 10^{11} \text{ km}^{-1}$ [1]. According to the regulation [2], which was based on the Particle Measurement Programme (PMP) recommendations [3, 4], the particle number system will sample from the Constant Volume Sampler (CVS) 10 to 20 tunnel diameters downstream of the exhaust gas inlet. The number measurement system will comprise a sample pre-conditioning unit/system (or volatile particle remover) upstream of a particle number concentration measurement device. A particle size pre-classifier (e.g. cyclone, impactor) prior to the inlet of the sample pre-conditioning system is recommended. The sample pre-conditioning system shall:

- Be capable of diluting the sample in one or more stages to achieve a particle number concentration below the upper threshold of the single particle count mode of the particle number counter (usually $10^4 \text{ \#/cm}^3$) and gas temperature below 35°C at the inlet of the counter.
- Include an initial heated dilution stage which outputs a diluted sample at a temperature of $150\text{--}400^\circ\text{C}$ and dilutes by a factor of at least 10.
- Achieve $>99\%$ reduction of an aerosol comprising 30 nm tetracontane ($\text{CH}_3(\text{CH}_2)_{38}\text{CH}_3$) particles (C40) with inlet concentration of $>10^4 \text{ \#/cm}^3$ by means of heating and reduction of partial pressures of the tetracontane.
- Achieve a particle number concentration reduction factor (*PRF*) for particles of 30 nm and 50 nm electrical mobility diameters, that is no more than 30% and 20% respectively higher, and no more than 5% lower than that for particles of 100 nm electrical mobility diameter. Initially it was required to achieve greater than 60, 70 and 80% non-volatile particle penetration at 30, 50 and 100 nm particle diameters respectively. However, it was found that it was difficult for labs to validate the operation of their instruments [5] and this recommendation changed.

Manufacturers are obliged to provide certificates that confirm the compliance of their systems with the above mentioned requirements. The provided factors (e.g. *PRFs*) should be used by the labs to calculate the particle number emissions of the vehicles. The calibration procedure was recently described in [6]. However, it is also required by labs to validate the proper operation of their instruments within six (or twelve if there are temperature monitoring alarms) months before the emissions test. Although the validation procedure is similar to the calibration procedure, there are two important differences:

- The validation procedure needs to be conducted only at the settings that the system will be typically used. In contrast, the calibration procedure needs to be conducted at the whole operation window of the system.
- The average of the factors that will be calculated by the validation procedure needs to be within $\pm 10\%$ of the manufacturer's average. If it is not, the system cannot be used for testing. If it is, the system can be used for testing, but the manufacturer's (calibration) average factor will be used for the calculations of the number emissions (and not the factor from the validation procedure).

In the following, various sample pre-conditioning systems are characterized. These include the Solid Particle Counter (SPCS) from Horiba, the NanoMet-C from Matter Eng., the ejector diluter and the thermodenuder from Dekati. Most of the systems were prototypes or were bought before the Euro 5/6 regulation and there were no certificates. Thus, this

study is not a validation of the systems, but application of the validation procedures. Terms like dilution factor, penetration, particle concentration reduction factor and volatile removal efficiency are defined. Issues that should be taken into account during these validation procedures are discussed. The results are compared with results using heavy duty diesel engine particles. In this paper only the characterization of the sample pre-conditioning units of the particle number systems is discussed. Information about the calibration/validation of the particle number counters can be found elsewhere [7, 8].

EXPERIMENTAL METHODS

DEFINITIONS

Figure 1 shows a sample pre-conditioning system and the parameters necessary for its characterization. The following definitions apply in this text:

Dilution Factor (*DF*): The *DF* of a system that samples a gas *k* of mass flow rate $M_{1,k}$ and mixes it with a dilution gas *k'* of mass flow rate $M_{da,k'}$ is:

$$DF = \frac{M_{1,k} + M_{da,k'}}{M_{1,k}} \quad (1)$$

The sample gas *k* and the dilution gas *k'* do not have to be the same but usually they are gases with similar densities in order to avoid corrections for densities in the flow rate measurements. In addition, these gases should be of similar properties with the exhaust gas so usually air or N_2 is used.

Equivalently, instead of flow rate measurements, gas concentration measurements can be used (e.g. with calibration gases like HC, CO in nitrogen etc). Assuming that a gas *j* enters the system with concentration $G_{1,j}$ (in the sample mass flow rate $M_{1,k}$) and concentration $G_{2,j}$ is measured at the outlet, then the dilution factor *DF* can also be calculated as:

$$DF = \frac{G_{1,j} - G_{da,j}}{G_{2,j} - G_{da,j}} \quad (2)$$

Where $G_{da,j}$ is the concentration of gas *j* at the dilution gas. The carrier gas $G_{1,j}$ should have properties similar with the exhaust gas (air) otherwise the measured *DF* might be different from the real one [9].

Penetration (*P*), Losses (*L*): Assuming that non-volatile (solid) particles of diameter d_i with concentration $N_{1,di}$ are contained in the sample gas and concentration $N_{2,di}$ is measured at the outlet, then the penetration of the system for the particles of diameter d_i is:

$$P_{di} = \frac{N_{2,di}}{N_{1,di} + N_{da}(DF - 1)} DF \quad (3)$$

Where N_{da} are the particles at the dilution gas. It must be emphasized that the total concentration of particles at the dilution gas must be taken into account for the calculation of the penetration and not only the concentration of particles with diameter d_i . However, it is very important that the concentration of particles in the dilution gas is zero, otherwise it is very difficult to correctly take into account their effect on the penetration. For example, the penetration of a system at 30 nm will be overestimated if the dilution gas contains particles of diameter >30 nm, as usually the penetration of the number systems at bigger diameters is higher. The losses L of the system are given:

$$L_{di} = 1 - P_{di} \quad (4)$$

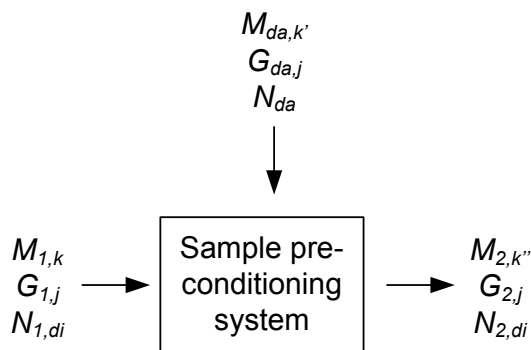


Figure 1: Parameters necessary for the characterization of a sample pre-conditioning system.

Particle Number Concentration Reduction Factor (PRF): A more simple definition for the “particle dilution factor” (as it is some times called) is the *PRF* (for particles of diameter d_i):

$$PRF_{di} = \frac{N_{1,di} + N_{da}(DF - 1)}{N_{2,di}} = \frac{DF}{P_{di}} \quad (5)$$

As mentioned above, it must be ensured that the contribution of the dilution air particles is negligible. In this case, Eq. (5) simplifies to the definition given by the legislation, where no *DF* is required:

$$PRF_{di} = \frac{N_{1,di}}{N_{2,di}} \quad (6)$$

In case of contaminated dilution air, Eq. (6) gives 1% error when the dilution air has 0.5 #/cm³ (assuming inlet concentration 5x10³ #/cm³ and *DF* 100). The legislation requires that the ratio of 30 nm *PRF* to 100 nm *PRF* (normalized *PRF*₃₀) is within 0.95 and 1.3 and the normalized *PRF*₅₀ is within 0.95 and 1.2.

Volatile Removal Efficiency (VRE): The Volatile Removal Efficiency (*VRE*) of a system for (volatile) particles of a specific diameter d_i is practically given by Eq. (4). If the dilution gas contains volatiles or non-volatile particles the *VRE* will be underestimated. For this reason it must be ensured that the dilution air is free of volatile or non-volatile particles. In this case *VRE* is given, in accordance with the legislation, from the equation:

$$VRE_{di} = 1 - \frac{N_{2,di}}{N_{1,di}} DF \quad (7)$$

According to the legislation, the system should be checked with the minimum *DF* and a concentration of >10⁴ #/cm³ of at least 30 nm C40 particles. Note that, by definition, the *DF* is required. However, as it might not be available for some systems (as it is not required by the legislation), it can be replaced with the 30 nm *PRF* without significant error.

The terms *P*, *L* and *VRE* refer to a specific particle size but the subscript d_i will be omitted in this paper. No background correction has been applied to the results of this paper. As mentioned previously, the effect should be negligible.

DESCRIPTION OF THE SET UP

Measurement of *DF* with flow rates: The *DF* of the ejector diluters was measured with a TSI 4040 flow meter (accuracy 2% or 0.05 lpm whichever is greater) by measuring the sample and the total outlet flow rate according to the procedure described in [9].

Measurement of *DF* with gases: The *DFs* were measured with 1.52% (±2%) propane in N₂ gas. An AVL CEB II FID analyzer was used to measure the diluted gas (repeatability ±5 ppm). The flow had to be restricted to 3 lpm to permit the measurements downstream of the Solid Particle Counter System (SPCS) from Horiba (Figure 2). This throttled line was used also for the other systems. Comparison of the “flow restricted” value to the non-restricted showed that there was no difference (only 2 ppm difference of a measurement at 260 ppm). The background was measured at the beginning of the tests and was found around 20 ppm. This background was taken into account in the calculations of the *DFs*. The uncertainty of the *DF* measurements with gases (variation of the background and the measured diluted value over two days) was ±5%. The inlet pressure and temperature were measured with a TSI 4040 flow meter (accuracy ±1°C and ±1 kPa respectively) connected at the inlet of the sample pre-conditioning system.

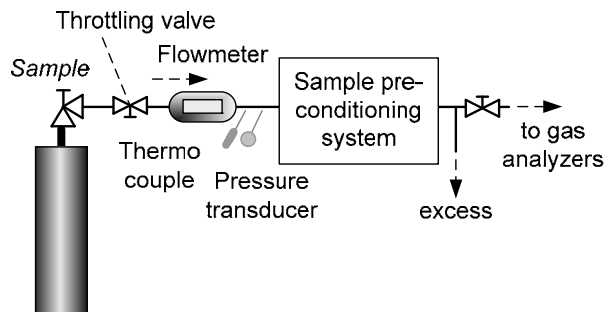


Figure 2: Set up for the *DF* measurements with gases.

Monodisperse measurement of *P, L, PRF, VRE*: The systems were characterized with monodisperse aerosol at diameters 30, 50, 70 and 100 nm. The set up can be seen in Figure 3a. Polydisperse particles were produced by various generators (see below). A differential mobility analyzer (DMA) (TSI, Model 3080L or 3085N) was used to separate monodisperse particles. Only stable concentrations above $5 \times 10^3 \text{ \#}/\text{cm}^3$ at the inlet of the sample pre-conditioning systems were used to calculate the penetration. For the volatile removal efficiency tests, the concentration was $>10^4 \text{ \#}/\text{cm}^3$. A TSI Condensation Particle Counter (CPC) 3025A (50% cut-point at 3 nm) was used to measure upstream and downstream of the system under evaluation. The flow was compensated with a pump for most tests. A TSI CPC 3790 (50% cut-point at 23 nm) was used upstream of the sample pre-conditioning system to check the stability of the generator.

Polydisperse measurement of *P, L, PRF, VRE*: A Scanning Mobility Particle Sizer (SMPS) (TSI 3936 (3080L+3010) or a nano-SMPS (3085N+3025A)) was used upstream and downstream of the systems under investigation (Figure 3b). The sheath/sample flowrates were 10/1 and 15/1.5 respectively. In most cases a CPC 3790 (1 lpm) or a 3025A (1.5 lpm) was used interchangeably with the SMPS in order to ensure that by changing the instruments' position the pressures and the flowrates were not affected.

At least two repetitions were conducted upstream and downstream to ensure stable conditions. Most of the tests were repeated another day to check the repeatability, which will be reported in the tables of the "Results" section.

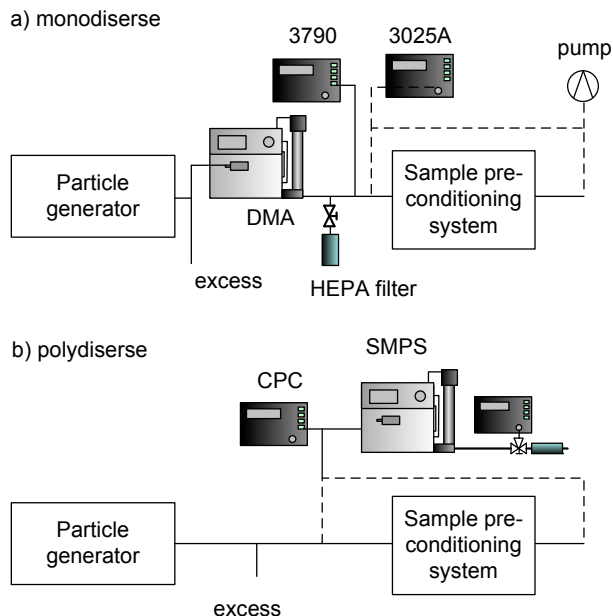


Figure 3: Set up for *P, L, PRF, VRE* a) monodisperse b) polydisperse measurements. For the Nanomet-C and ejector diluter tests a thermodenuder was installed downstream of the particle generator.

DESCRIPTION OF THE SYSTEMS

Dilution air: The dilution air line for all systems was filtered with active carbon and HEPA filters, thus the need for background correction should be negligible.

Particle generators: A Horiba tetracontane (C40) particle generator VGU (evaporation-condensation technique) produced volatile particles. For the 100 nm non-volatile particles the Horiba NaCl atomizer generator LCU was used (nebulizer). The prototype JRC NaCl generator (evaporation-condensation technique) gave peaks in the range of 15-50 nm and it was used for the 30, 50 and 70 nm measurements.

An IVECO Cursor 8 (7.8 l, 6 cylinder, 4 valves/cylinder) Euro III engine without any after-treatment devices or with a continuous regenerating filter was used to produce diesel particles (non-volatiles or volatiles respectively).

Old NanoMet-C: An older version of the NanoMet-C (Matter Engineering) was used during the light duty PMP inter-laboratory exercise as the reference (golden) sample pre-conditioning system. The components of the old NanoMet-C comprised: primary hot rotating disk diluter (150°C), 1 m line, evaporation tube (150°C) and secondary simple mixer cold diluter. The primary *DF* was controlled by changing the rotation of the primary diluter. More information about the system can be found in [5]. The only difference with that study is that no CPC was installed upstream of the ET.

NanoMet-C: A new rotating disk based system from Matter Eng. was used. This system consisted of a primary rotating disk diluter heated at 150°C, a 1 m line, an evaporation tube at 300°C and a secondary simple mixer diluter. Both diluters had adjustable *DFs* [10].

SPCS: The Solid Particle Counting System (SPCS) from Horiba consisted of a primary hot Horiba Wide Range Continuous Diluter (WRCD) at 170°C, an evaporation tube at 350 °C and a secondary diluter at ambient temperature. A more analytical description of the system can be found in [11, 12, 13]. The particle losses according to the manufacturer are <5% for polydisperse particles and <15% for monodisperse particles [14].

Evaporation chamber: An evaporation chamber (7 cm length, 3.5 cm inner diameter) from Dekati Ltd. was used. The temperature was set to 330°C. The volume was 67 cm³ and for a flow rate of 2.6 lpm (the flow rate of the modified ejector diluter downstream of the evaporation chamber) the residence time was 0.8 s.

Ejector diluter: In ejector diluters pressurized dilution gas flows through a ring orifice in the periphery of a nozzle. The under-pressure developed (as dilution air is accelerated in the orifice) draws in sample gas that flows in the nozzle and, consequently, the dilution stage is self-sucking system. Typical diluters operate at a *DF* of 10, the exact value of which depends on the geometrical characteristics of the diluter, the composition of the sample and the dilution gas, and the operation conditions, i.e. pressures and temperatures of the raw sample, the dilution gas and the diluted sample [9].

In order to predict and correct for these changes, a model was developed to calculate the actual value of the *DF* as a function of the ejector operating parameters [9]. The model assumes compressible flow which reaches supersonic velocity at a variable cross-section duct. This terminates with a normal shock wave occurring at the mixing area. According to this model, the theoretical corrections coefficients that should be applied for the different sample and/or dilution air temperatures and pressures are shown in Table 1.

The primary diluter was used with dilution air at 150°C and with a surrounding blanket at 150°C. A correction factor of 0.98 should be applied for the blanket, a correction factor of 0.94 should be applied for the dilution air (the dilution air heats also the sample). It should be noted that the ejectors are sensitive to pressure changes. For example, according to the model, a 5 kPa under-pressure at the inlet of the diluter needs a correction of 1.14 of the nominal *DF*. For the secondary diluter downstream of the evaporation tube, due to the high sample temperature, a correction of 1.19 to 1.38 should be applied (depending on the sample temperature). In these experiments a correction of 1.3 was used as the temperature upstream of the secondary diluter was measured around 250°C.

The particle losses in the range of 20-500 nm should be negligible (<5%) according to [15], where diesel particles from a light-duty Euro 3 vehicle were measured.

Table 1: Correction coefficients for ejector diluters for different pressure and temperature conditions according to the model in [9]. *s*=sample, *da*=dilution air, *m*=mixture, *p*=pressure, *t*=temperature. Numbers in parenthesis are estimations from the model.

<i>p(s)</i>	<i>t(s)</i>	<i>t(da)</i>	<i>t(m)</i>	Correction factor	Comments
kPa	°C	°C	°C	-	-
100	17	17	(17)	1.00	Reference conditions
100	100	17	(24)	1.12	At CVS (high temperature modes)
100	150	17	(27)	1.19	Downstream of evaporation tube (cooled)
100	300	17	(36)	1.38	Downstream of evaporation tube
100	17	150	(136)	0.84	Heating of dilution air
100	100	150	(145)	0.94	Heating of dilution air, effect on sample
97	17	17	(17)	1.08	CVS, under-pressure
95	17	17	(17)	1.14	CVS, 90 lpm pump under-pressure
100	17	17	150	0.98	Blanket heating

Dual ejector system: In this system the first dilution was conducted with a heated ejector diluter (dilution air 150°C and blanket 150°C). The diluted sample was further heated in an evaporation chamber (330°C) and then was further diluted by a secondary ejector diluter at ambient temperature.

Thermodenuder (TD): A thermodenuder (TD) from Dekati Ltd. was used. The temperature of the heater was set to 300°C (residence time 0.3 s for 10 lpm flow rate). The carbon section had an annular design, i.e. the carbon was placed at both sides of the sample flow. The inner cylinder was cooled by forced convection (air in these experiments) and the outer by natural convection. The residence time in this section was 2.7 s (for a flow rate of 10 lpm). The particle losses L for 250°C according to the manufacturer (measured with NaCl) should be [15]:

$$L_{di} = -9.7 \ln d_i - 0.5Q + 68 \quad 30 < d_i < 70 \text{ nm} \quad (8a)$$

$$L_{di} = -0.5Q + 28.7 \quad 70 < d_i < 500 \text{ nm} \quad (8b)$$

Where d_i is the particle size [nm] and Q is the flow rate through the thermodenuder [lpm] (10-20 lpm).

Ejector with TD system: This system comprised of a heated ejector diluter (dilution air and blanket at 150°C) and a thermodenuder (TD) (see above).

RESULTS

The results of the measurements will be reported in this section separately for DF , P , PRF and VRE .

DILUTION FACTOR (DF)

Old NanoMet-C: The DF was measured at 20% and 60% rotation. The secondary DF was 5.2 according to the manufacturer. Table 2 shows the measured DFs (with gases) and the values from the manufacturer at various pressures (see Figure 2 for the set up). A 8.5 kPa under-pressure had as an

effect a 25-30% increase of the measured DF (e.g. from 250 to 317). These results indicate that the dilution value that is given by the manufacturer should also take into account the pressure of the sample. In another study it was also indicated that the temperature of the sample should be taken into account [16].

NanoMet-C: The primary DFs were measured at 20%, 50% and 80% rotation and the secondary DF was set at 6 or 11. All measurements were conducted at ambient pressure. The results showed a generally good agreement ($\pm 10\%$) between the measured and the manufacturer's values (Table 2).

SPCS: Table 2 shows the measured DFs and their differences compared to the software values. The differences were less than $\pm 5\%$; results in agreement with the manufacturer's data [11, 14]. The under-pressure had also very small effect on the DF .

Ejectors: The DF of the ejector diluters was determined by measuring sample and total flow rates at ambient temperature and pressure with a 4040 TSI flow meter [9]. The first diluter (#1, 60242) had a DF of 10.2 at ambient conditions, while the second diluter (#2, 60244) had a dilution ratio of 11.4. For the dual heated system correction factors of 0.98 (blanket), 0.94 (dilution air) and 1.3 (hot sample at second diluter) were used (see Table 1 for corrections). Table 2 shows the measured with gases DFs (see Figure 2 for the set up) and the results from the model (in the "Software" column). If the nominal DFs were used for the dual heated system the results would be very different from the real (measured with gases) values. The measurements showed that there is a significant effect of both the pressure upstream of the ejector diluters and the temperature of the dilution air. It is very important for the users of the ejector diluters to apply the correction factors given in Table 1. The model takes into account this pressure and temperature correctly (differences $\pm 5\%$, see [9]).