PEMs 4Nano

Portable Nano-Particle Emission Measurement System

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Written By	Thomas Maier (HORIBA Europe GmbH)	2018-02-22
Checked by	Thomas Maier (HORIBA Europe GmbH) (WP2 leader)	2018-02-23
	Florian Hüwe (HORIBA Europe GmbH)	2018-02-25
Approved by	Hans Georg Horn (TSI)	2018-02-26
	Cristian Focsa (ULL)	2018-02-26
	Marcus Rieker (HORIBA) - Coordinator	2018-02-27
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Publishable Executive Summary

Objectives

To support PEMs4nano emission measurements, which will be performed at the Single-Cylinder- and Multi-Cylinder test-benches at the project partner Bosch, as well as Dyno- and PEMS-tests to be performed at IDIADA, PN-instruments with extended capability of Sub-23 nm particle counting need to be available.

For these purposes, HORIBA Europe is designated to create a laboratory 10 nm particle counting system "PEMs4Nano LabSystem" which will be presented in this D2.04 report, as well as a subsequent "PEMs4Nano PEMS-System" by the following deliverable D2.07.

After enabling the LabSystem for Sub 23nm particle number measurements by equipping it with a catalytic stripper as well as the 10 nm CPC created by TSI in D2.02, an initial calibration of the instrument had to be established and carried out to document the systems performance as well as to determine the respective calibration of PCRF (particle concentration reduction) factors needed for the calculation of an engine's particle number emission levels.

After this initial modification and calibration of the PEMs4Nano LabSystem, the instrument will be transferred to – and will be installed at the PEMs4Nano project partner Bosch Single-Cylinder testbed facilities in Renningen (Germany) for first investigations of engines small particle emissions and respective influences on instrument and engine performance.

As the PEMs4Nano proposal is projecting Month 17 (February 2018) as a target for completion of the above described LabSystem modifications, investigations and calibrations, this report is documenting the calibration procedure as well as the calibration results. The instrument is ready for shipment to Bosch, which will be performed together with supported installation and initial operation on-site in March 2018.

Methods

For creating the PEMs4Nano 10 nm laboratory prototype, both the modification of the CPC installed in the SPCS, as well as the modification by replacing the ET to a CS were performed on the premise of maintaining best consistency and interchangeability with current 23 nm SPCS systems under hardware and calibration aspects.

The specific procedures of PCRF calibration performed by HORIBA for SPCS-2x000's VPR as well as DSU calibration will be described, explained and analyzed in detail. Moreover, impacts and possible improvements for PCRF calibration of sub-23 nm systems will be discussed.

The original \overline{PCRF} -average calibration values of PMP are calculated as average of three different size setpoints PCRF (D_P)'s. Complementary to the original PMP PCRF definition using 100 nm, 50 nm and 30 nm values, two more average PCRF definitions will be used in this report, also including 15 nm and/or 23 nm values.

Results

According to the different possible definitions for the calculation of the \overline{PCRF} -average, results are shown drawn in Figure 1-1. $\overline{PCRF_{30-100}}$ is the PMP standard \overline{PCRF} , averaging 100 nm, 50 nm and 30 nm measurements. $\overline{PCRF_{23-100}}$ additionally includes 23 nm and $\overline{PCRF_{15-100}}$ additionally includes 23 nm and 15 nm, thus leading to higher factors due to increased particle losses going to smaller particle sizes. PEMs4Nano of these different definitions are drawn in blue nuances for the PEMs4Nano LabSystem, whereas the HOR-results of the original nonmodified, ET-equipped SPCS are drawn in grey for comparison.





Figure 1-1: PEMs4Nano LabSystem – PCRF calibration – Averaged PCRF values over all dilution-settings (Dil) for different definitions of \overline{PCRF}_{xx-100} .

Left Graph: Absolute values; Right Graph: Values normalized with respective dilution-ratio.

Grey bars: Original, ET-equipped, non-modified SPCS-2100 system; Blue bars: CS-equipped, modified PEMs4Nano LabSystem.

Considering specifications of PMP-based regulations for PN-counting (e.g. ECE-R84, ECE-R49), the modified PEMs4Nano LabSystem still is fully compliant to the PMP-recommendations for the VPR despite extra losses induced by the installed CS compared to the original ET.

New calibration factors according to three introduced, different definitions for a \overline{PCRF} -average for the VPR ($\overline{PCRF_{30-100}}$, $\overline{PCRF_{23-100}}$, $\overline{PCRF_{15-100}}$) as well as for the DSU ($\overline{PCRF_{DSU,30-100}}$, $\overline{PCRF_{DSU,23-100}}$, $\overline{PCRF_{DSU,15-100}}$) have been established and will be supplied with the prototype. With the standard PMP definition being programmed into the system, an easy re-calculation to the extended definitions of the average can be performed for discussions of any future regulatory definition.

Dilution (Dil)	PND1	PND2	PCRF ₃₀₋₁₀₀	PCRF ₂₃₋₁₀₀	PCRF ₁₅₋₁₀₀
150	10	15	175,09	185,27	198,27
300	20	15	359,80	379,43	396,03
750	50	15	945,36	995,31	1068,66
1500	100	15	1841,54	1961,60	2069,10
3000	200	15	3907,26	4091,35	4249,86
DSU	x 1	0	12,16	12,97	13,84

Table 1-1: PEMs4Nano LabSystem – Summary of VPR and DSU calibration – Final PCRF factors to be programmed to SPCS.

Considering any final definitions of extended exact $\overline{PCRF_{xx-100}}$ -factors also including smaller particle sizes, it should be suggested that PCRF sizes to be included should deliberately be weighted considering statistics of real emitted size distributions of currently prevailing modern engine concepts, also regarding the respective influence on the PN value by weighting with the overall PNCS size dependent efficiency.



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1 Introduction

To support PEMs4nano emission measurements, which will be performed at the Single-Cylinder- and Multi-Cylinder test-benches at the project partner Bosch, as well as Dyno- and PEMS-tests to be performed at IDIADA, PN-instruments with extended capability of Sub-23 nm particle counting need to be available.

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2 PMP solid particle counting method & challenges on 10 nm measurement

2.1 Overview on PMP solid particle counting

According to Euro 5b&6 regulations, the limit for light-duty (LD) diesel vehicles is $6x10^{11}$ particles emitted per km for type approvals/initial-registrations starting from 2011/2013. The PN limits subsequently were expanded to direct-injecting gasoline engines in two stages, which may emit a maximum of $6x10^{12}$ particles per km with Euro 6b becoming valid in 2014/2015, and $6x10^{11}$ particles per km equally with Euro 6c starting from 2017/2018. For heavy duty (HD) diesel vehicles, a limit of $6/8x10^{11}$ particles/kWh is applied with Euro VI since 2013/2014.

For measuring this number of emitted particles, the UNECE Particle Measurement Programme (PMP) previously developed a measurement procedure for the quantification of solid, non-volatile particles of about 23 nm and larger. This procedure was subsequently adopted into the European Directives ECE-R83 for light-duty vehicles and into ECE-R49 for heavy-duty applications. Although these both are the obligatory regulations defining PN measurements for emissions certification in Europe, the term PMP will also be used synonymously in the following report referring to the respective PMP proposals of PN instruments adopted in these regulations.

Figure 2-1 illustrates the schematic structure of a setup for PMP particle counting, composed of an upstream engine exhaust dilution system and a PMP Particle Number Counting System (PNCS) sampling from this dilution system.



Figure 2-1: Schematic of a setup for PMP particle number measurement.

2.2 Exhaust-dilution systems

Prior to sampling by a PMP particle number counting system, the engine exhaust gas first must be pre-diluted by an exhaust-dilution system. This can be by means of a proportional-dilution system (CVS, PFDS) for certifications appliances. Alternatively, raw-exhaust dilution is often used for R&D purposes (but currently not yet approved for certification measurements).

2.2.1 Proportional exhaust-dilution regarded by PMP (CVS, PFDS)

LD and HD applications allow a conventional full-flow dilution system (CVS). Here, the whole exhaust stream emitted from the engine is directed into a dilution tunnel. In the tunnel, the exhaust is mixed with dilution air which was previously cleaned by activated carbon and HEPA filters (High-Efficiency Particulate Air Filter). The total flow of diluted exhaust gas is then kept constant, usually by using critically operated venturi nozzles, which will be chosen to adjust the flow to reach a minimal dilution of approx. 1:5 under expected engine full load conditions.

This system is often referred to as CVS (Constant Volume Sampling) system because the total mass flow of diluted exhaust gas through the dilution system - as well as the exhaust samples for the determination of gaseous emission components (CO, CO2, HC, NOx) extracted though a sample venturi – both are kept constant by critical flows and thus the sample flow fraction always is proportional to the tunnel flow. The resulting dilution rate in the tunnel is passively variable during a test because of the exhaust gas mass flow changes depending on the engine operating point, but the total mass flow through the CVS remains largely constant.



For HD applications only, also Partial Flow Dilution Systems (PFDS) are allowed alternatively due to their lower cost and size compared to full flow dilution of the major HD engine exhaust streams. Here, a sample portion $q_{mp}(t)$ is withdrawn from the raw exhaust gas, which is actively adjusted to be proportional to the total exhaust gas mass flow $q_{mew}(t)$ of the engine. Consequently, these systems are called partial flow dilution systems. Actively controlling this proportionality in terms of accuracy and temporal response is the biggest challenge for PFDSs, especially during highly transient cycles. For this, fast real-time measurements, in particular of the exhaust gas mass flow, as well as a rapid change and proportional adaptation of the mass flows in the PFDS are necessary.

2.2.2 Direct- / raw-exhaust sampling & dilution (RAW)

A direct, raw-exhaust dilution (RAW), is mostly realized by using constant dilution factors, either by an additional pre-dilution-stage (PND0, DSU for HORIBA SPCS with a dilution ratio of 1:10) or by appropriate construction of the PND1 of the PMP system (higher dilution factors, high-temperature resistance). This kind of dilution is challenging in terms of pressure and temperature conditions as well as their temporal gradients in the raw exhaust stream.

In the evaluation of dynamic measurements, direct sampling and its analysis additionally has very high requirements on the temporal synchronization of the measured particle concentration with the exhaust gas flowrate, and its absolute accuracy especially during low-load and transient operation.

Direct-sampling methods are currently not yet approved for certification purposes but are evaluated in the PMP working group for HD applications. Moreover, they are standard procedure for PEMS-PN measurements as a proportional dilution is not applicable here in terms of weight and size restrictions in mobile applications.

2.3 PMP solid particle counting methodology

For means of solid particle number counting, a sample of diluted exhaust is taken out of any of the above exhaust dilution systems and lead via a Particle Transfer Tube (PTT) to the PMP particle number counting system (PNCS), which itself consists of the Volatile Particle Remover (VPR) and the subsequent Condensation Particle Counter (CPC).

2.3.1 Particle Transfer Tube (PTT)

The so-called Particle Transfer System (PTS) includes a Particle Sampling Probe (PSP) in the exhaust dilution system as well as the Particle Transfer Tube (PTT), i.e. the line between probe and VPR. The sampling position should be at a distance of 10 - 20 tunnel diameters after the exhaust gas entry into the dilution tunnel to extract a homogenously diluted sample. In the regulations ECE-R83 & R49 it was specified that the PTS should have an inside diameter of ≥ 8 mm, and that the residence time of the particles should not be greater than 3 seconds at a maximum Reynolds number of 1700 (laminar flow) before the sample enters the VPR.

2.3.2 Volatile Particle Remover (VPR)

Conditioning and diluting the sampled aerosol, the VPR must remove liquid volatile exhaust gas components (e.g. water vapor, unburned hydrocarbons, H_2SO_4 or SO_x) from the aerosol stream, components which might occur as droplets or condensed layers on solid particles. Moreover, any (re-)condensation or (re-)nucleation of these volatile components needs to be prevented before the solid particle number is quantified by the CPC. Recondensation is prevented by heating and dilution only in conventional PMP 23 nm systems, without physically or chemically removing the vaporized compounds. Therefore, in a standard VPR, the particle stream is treated by the following steps:

- 1. The sample first is diluted hot in the first Particle Number Diluter (PND1, dilution > 1:10, dilution up to 1:100, T > 150°C)
- 2. Afterwards, the volatile deposits are evaporated into the gas phase by the Evaporation Tube (ET, 300-400°C, standard 350°C).
- 3. The sample then is diluted once again in the second Particle Number Diluter (PND2, dilution 1:10-15) to prepare it for final counting. Here, cooling by dilution is necessary to avoid any heterogeneous or



homogeneous re-condensation or nucleation of the vapor phase volatile components, in order to prevent a distortion of the PN particle count by volatile artifacts.

Besides this removal of volatile particles and/or volatile layers on the solid particles, the overall dilution must be suitable to achieve a VPR outlet particle concentration being in the allowable concentration range of the succeeding CPC under all operation conditions during the performed emissions test.

Sub-23 nm measurements are more prone to the described volatile artifacts. More sophisticated VPR principles for R&D are Thermo-Denuder- (TD) or Catalytic-Stripper-concepts (CS) which evaporate as well as physically and chemically remove the volatile components from the aerosol stream (instead of heating and dilution only). Thus, these two principles decrease the risk of any re-nucleation artifacts and therefore are predestined for sub-23 nm measurements.

2.3.3 Condensation Particle Counter (CPC)

The remaining solid particles are finally detected by a Condensation Particle Counter (CPC). Here, nanoparticles that are too small to be directly detected by optical means ($D_P \approx 23 - 200 \text{ nm}$) are grown to a size-range of > 1 µm using defined saturation- and supersaturation-steps, with particles then becoming optically detectable:

- 1. In the condenser-stage, the particle stream first is transferred though channels in a heated, Butanolsoaked wick and thus becomes saturated with Butanol vapor (for a TSI 23 nm CPC100: $T_{cond} \sim 38,5^{\circ}$ C).
- 2. Then during a subsequent cooling of the saturated aerosol in the condenser-stage the aerosol with its butanol vapor gets supersaturated in a defined way (for a TSI 23 nm CPC100: $T_{sat} \sim 30.8^{\circ}$ C).
- 3. As an effect of the supersaturation, the nanoparticles act as condensation nuclei for the Butanol vapor and grow to the size range > 1 μ m. After this, they can be individually detected in the succeeding optical stage.

The degree of supersaturation created through the condenser and saturator temperature setpoints determines the size-dependent particle growth and thus the CPC counting behavior. For PMP, this so-called cut-off efficiency should be 50 ± 12 % at 23 nm and > 90 % at 41 nm. CPCs meeting this specification often are referred to as engine exhaust CPCs (EECPCs).

In the optical cell, the grown particles are detected individually by forward-scattering of a laser beam, sensed via a fast photodetector unit and counted (N) via fast comparator & FPGA circuits. Together with the flow-rate \dot{V} though the CPC – which is typically determined by a critical flow orifice and respective pressure measurements – the final concentration reading of the CPC will be reported as:

$$c_{\rm CPC} = \frac{\Delta N}{\Delta t} * \frac{1}{\dot{V}} * k * k_{coincidence} \ [\text{#/cm}^3]. \tag{Eq. 2-1}$$

Here, k is the CPC calibration factor (see section 2.4.2) and $k_{coincidence}$ a correction factor correcting coincidence effects. These are caused by high particle concentrations leading to detector dead-times as two particles being in the optical volume at the same time cannot be discriminated (the factor is determined using actual or average pulse width times).

2.4 Calibration of a PMP system

In contrast to standard calibration procedures used for gas analyzers – which typically are performed daily with calibrated gases that can be stored in gas bottles at the test bench – calibrating and testing a PMP system poses a major challenge. Instead of using a stored "calibration gas", an aerosol only can be produced directly during the calibration process by a particle generator, which then needs to be processed in a defined and reproducible manner in terms of size and particle concentration.

This calibration must be performed at least every 12 months and, due to the complexity of the calibration and the necessary setups, is normally performed by the manufacturers of particle number measuring systems:



- It requires the elaborate provision and use of model aerosols (e.g. carbon particles from propane flame or graphite spark generators, NaCl, Emery Oil),
- a particle size selection and particle dilution(s),
- as well as referencing against an electrometer (primary method) or reference CPC (secondary method).

The calibration of a PMP system is performed component by component:

- 1. On the VPR side, the particle penetration for 30, 50 and 100 nm particles is determined, resulting in a mean penetration **PCRF factor** (details in section 2.4.1).
- 2. On the part of the CPC, the counting efficiency at 23 nm and 41 nm is checked (**cut-off**) and the concentration linearity is measured which results in a CPC calibration factor (**k-factor**, see section 2.4.2).

2.4.1 PMP VPR-calibration (PCRF-factor)

The PCRF-factor describes the ratio of particle number concentrations before $(N_{in}(D_P))$ and after $(N_{out}(D_P))$ the passage through the VPR of the particle number counting system at different particle diameters D_P . Thus, the PCRF includes both the selected dilution factor as well as losses caused by deposition processes which particles will undergo during their passage from PNCS inlet to CPC inlet.

The *PCRF* (D_P) for each particle size then is calculated as shown in equation (Eq. 2-2). Particle sizes D_P used in PMP are 30 nm, 50 nm and 100 nm.

$$PCRF(D_{\rm P}) = \frac{N_{\rm in}(D_{\rm P})}{N_{\rm out}(D_{\rm P})}.$$
(Eq. 2-2)

The ratio of these three PCRF values is limited by the respective regulation. The PCRF for 30 nm is allowed to be 30% higher and 5% lower than the PCRF for 100 nm. For the PCRF of 50 nm the limits are 20% and 5% respectively.

For calculating the particle number concentration $c_{PNCS,inlet}$ at the PNCS inlet, the experimentally determined concentration of the CPC (c_{CPC}) then is multiplied by the average calibrated \overline{PCRF} , thus taking into account the dilution as well as the average particle losses in the VPR:

$$\overline{PCRF} = \frac{PCRF(30nm) + PCRF(50nm) + PCRF(100nm)}{3}.$$
 (Eq. 2-3)

$$c_{PNCS,inlet} = \overline{PCRF} * c_{CPC} . \tag{Eq. 2-4}$$

During initial calibration of a PMP system, this \overline{PCRF} value has to be determined for each available dilution setting of the PNCS. During annual maintenance of the system, it is allowed to determine the \overline{PCRF} value of one dilution setting only in case this result still is in the allowed limits (±10 % of previous calibration). In this case, a full recalibration of all \overline{PCRF} values is not necessary.

In addition, the removal of volatile components is checked by confirming a removal of tetracontane particles $(CH_3(CH_2)_{38}CH_3)$ with an efficiency higher than 99%.



2.4.2 PMP CPC-calibration (η_{CPC} , k-factor)

The cut-off characteristics of a CPC can be described as a size dependent detection efficiency $\eta_{CPC}(D_P)$. For calibration, the CPC under test will be measured against a reference $c_{Reference}(D_P)$ instrument with both instruments sampling the same monodisperse model aerosol (originally PAO-aerosol (Emery Oil) for TSI EECPCs, Cast-Aerosol for PEMs4Nano CPC, ...). In case of a primary calibration, the reference instrument will be a Faraday Cup Aerosol Electrometer (FCAE), where input particle concentration can be determined by measurement of an electrical current together with known particle charge and aerosol flow. In case of a secondary calibration, the reference instrument might be a second CPC, which however was calibrated to a FCE.

$$\eta_{CPC}(D_P) = \frac{c_{CPC}(D_P)}{c_{Reference}(D_P)}.$$
(Eq. 2-5)

For usage in a PMP-compliant particle number counting system, two points of the CPCs detection efficiency characteristic $\eta_{CPC}(D_P)$ need to be in the ranges specified in equation (Eq. 2-5), with the D₅₀ value being at 23 nm:

$$\begin{split} \eta_{CPC100}(23nm) &= 50\% \pm 12\% \text{ ; (D}_{50}) \\ \eta_{CPC100}(41nm) &\geq 90\% \text{ .} \end{split} \tag{Eq. 2-6}$$

Beside this cut-off characteristic, PMP-CPCs need to be tested for linearity over their specified concentration range $(0 - 10\ 000\ \text{#/cm}^2$, typically at 55 nm for PMP 23 nm CPCs), using at least six evenly distributed concentration setpoints. The resulting linear regression should have a minimal coefficient of determination R² > 0,97 and the reciprocal slope of the regression leads to the CPCs k-factor as an absolute concentration calibration factor (compare (Eq. 2-1)).

Additionally, ISO 27891 describes the procedure to measure single calibration data points efficiency $\eta_{CPC}(D_P)$, and it also gives criteria to determine the validity of a calibration data point measurement and methods to determine measurement uncertainty.

2.5 Calculation of engine PN emissions levels

Modal PN(t) emissions levels of an engine can be calculated taking into account the modal engine exhaust flow $\dot{V}_{exhaust}(t) = q_{mew}(t)$, the dilution factor $Dil_{\text{CVS/PFDS/DSU}}(t)$ of the primary exhaust dilution system as well as the calibration factors \overline{PCRF} for the VPR and k_{CPC} for the CPC:

$$PN(t) = \dot{V}_{exhaust}(t) * Dil_{CVS/PFDS/DSU}(t) * \overline{PCRF} * k_{CPC} * c_{CPC}(t).$$
(Eq. 2-7)

Special attention needs to be paid here for temporal synchronization of the single signals.

For calculation of the overall particle number PN_{DSU} during an emissions test using DSU raw-exhaust dilution, the respective modal data needs to be convoluted:

$$PN_{DSU} = \overline{PCRF} * k_{CPC} * \int \dot{V}_{exhaust}(t) * Dil_{DSU}(t) * c_{CPC}(t) dt.$$
(Eq. 2-8)



Using the proportional exhaust dilution of a CVS, the overall integration of PN(t) is easier as $\dot{V}_{exhaust}(t) * Dil_{CVS}(t)$ becomes constant by the CVS principle, leaving V_{CVS} as overall integrated volume flown through the CVS during an emissions test:

$$PN_{CVS} = \overline{PCRF} * k_{CPC} * \int \dot{V}_{CVS} dt * \int c_{CPC} dt =$$

= $\overline{PCRF} * k_{CPC} * V_{CVS,test} * \overline{c_{CPC}}$. (Eq. 2-9)

2.6 PMP PNCS: HORIBA MEXA SPCS-2x00 working principles

Figure 2-2 shows the detailed flow schematic of a standard HORIBA MEXA SPCS-2100 solid particle counting system, where the type number 2100 in the type designation stands for a SPCS system which is also capable of direct raw-exhaust measurements (compare section 2.2.2) making use of an extra 1:10 pre-dilution unit designated DSU (direct sampling unit). All MEXA SPCS-2x00 systems are fully compliant to PMP-based regulations. In Figure 2-2, basic PMP functional elements are additionally indicated by blue boxes comparable to the elements in Figure 2-1.

Before presenting the modifications of the system to be done for developing the PEMs4Nano 10 nm laboratory system capable of sub-23 nm measurements in section 2.7, the basic working principle of SPCS systems' components will be shortly introduced and explained in the following. For ease of understanding, this explanation will go from back-to-front looking at the aerosol stream, thus starting at the CPC as final particle detector.



Figure 2-2: Flow schematic of a standard HORIBA MEXA SPCS-2100 solid particle counting system (PMP 23 nm).



CPC

HORIBA MEXA SPCS-2x00 systems include a TSI CPC100, which is the OEM version of TSI's engine exhaust CPC (EECPC) series (like TSI3790/3791) which is optimized for operation in SPCS systems. Being a butanol full-flow CPC operating in single-count mode specified up to 10 000 particles/cm³, it fully complies with the above PMP specifications using a calibration with $D_{50} = 23$ nm (see (Eq. 2-6)).

Aerosol flow though the CPC is determined by an internal CFO (critical flow orifice), which obtains its vacuum by the SPCS vacuum supply, resulting in a flow of approx. 1 Slpm at (TSI) standard conditions of 294.3 K (21,1°C) and 101,3 kPa. The exact flow at actual sampling conditions is calculated by SPCS using the CPCs internal pressure sensor readings. Additional valves in SPCS are designated to allow PMP daily checks of 'CPC-Span' (sampling ambient particles) and 'CPC-Zero' (sampling HEPA-filtered air).

PND2

The second Particle Number Diluter in SPCS is regulated to a constant dilution ratio of DF = 1:15. Here, the diluters output flow is split to the 1 lpm sample flow entering the CPC and a ~ 14 lpm bypass flow drawn by CFO-3 in SPCS, leading to a flow of 15 lpm exiting the diluter. Using online flow-calculation of both of these critical flows (considering actual pressures and temperatures), the PND2's dilution air supply is maintained by MFC-3 set to 14:15 of this flow (~ 14 lpm). This results in the desired 1:15 dilution factor as well as an incoming 1 lpm aerosol flow drawn from the preceding evaporation tube. To increase accuracy, both CPC flows are calibrated to MFC-3 readings on a daily basis in SPCS ("CPC/CFO flow calibration").

EΤ

The evaporation tube in HORIBA SPCS systems is realized by a heated stainless-steel tube regulated to a wall temperature of 350 C, with an 1 lpm sample flow drawn by PND2.

PND1

The SPCS's first Particle Number Diluter is realized by HORIBA's patented "Wide-Range Continuous Diluter" (WRCD, patent WO2006086615A2), being capable of accurately adjusting a range of dilution factors from 1:10 to 1:200. Here in PND1, the online-determined dilution factor is calculated using the measured flow-rates of both incoming flows. The incoming aerosol flow is directly measured by a flow-orifice meter (FO-1, 0,10-0,44 NIpm) measuring the absolute and differential pressure as well as gas temperature over a small orifice (non-critical). This direct measurement of aerosol flow leads to a high accuracy of this diluter setup compared to differential diluters where measurement errors might multiply with the DF as sample flow needs to be differentially calculated. The PND1's dilution air flow necessary for the set dilution factor is established by MFC-1, and diluted with the aerosol flow after FO-1. The overall flow now exiting PND1 is composed of the ~ 1 NIpm flow into the ET as well as an additional bypass flow established by CFO-2 which is fed-up by MFC-2, with MFC-2 used for regulation of the preset & desired FO-flow. Example flows for a dilution of 1:10 range from approx. 0,44 NIpm entering through FO-1 and 3,56 NIpm entering for dilution via MFC-1. For a dilution factor of 1:200 these flows are maintained to 0,10 NIpm and 19,9 NIpm respectively (deviations to these exact absolute values will occur during SPCS operation, however relative factors will be maintained, resulting in a constant reproduction of the dilution factor during original calibration).

Cyclone

The shown HORIBA MEXA SPCS-2100 is equipped with a Cyclone between PTT and PND1 to remove large particles by inertial deposition. This prevents contamination of subsequent components without affecting particle number count as only particles in the micrometer range are separated from the aerosol flow.

PTT

To connect any SPCS to their respective Full-Flow-, Partial-Flow- or Raw-dilution system (CVS, PFDS, RAW/DSU), a heated Particle Transfer Tube (PTT) is used. In SPCS setups, this tube mostly has the length of ~ 4 m, consisting of a 8 mm/10 mm (I.D./O.D) conductive tube in a heating hose regulated to a temperature of 47°C to prevent condensation of exhaust components in the pre-diluted flow. Despite the small flow entering PND1-dilution in



SPCS, the flow drawn through the PTT is increased to ~ 10 lpm using an additional bypass line (CFO-1) to reduce transfer time and particle losses in the PTT while maintaining the PMP-requirement of laminar flow.

DSU

Direct raw-exhaust dilution can be realized using an additional HORIBA Direct Sampling Unit (DSU) in place of conventional Full-Flow- (CVS) or Partial-Flow- (PFDS) exhaust dilution systems. In the DSU, the 10 lpm diluted flow exiting to the PTT is fed up by a 9 lpm dilution flow established by MFC-61 in the SPCS main unit. Thus, an exhaust sample flow of 1 lpm as well the desired constant dilution factor of 1:10 is maintained. To reduce pressure fluctuations as well as overpressures induced by the connected engine exhaust line, the DSU is equipped with two decoupling stages each consisting of an orifice and a direct-spring overpressure-valve.

2.7 Challenges on sub-23 nm measurements for PMP instruments & approach for SPCS modifications to 10 nm laboratory counting system "PEMs4Nano LabSystem"

This section shortly summarizes the challenges for a PMP instrument during sub-23 nm measurements as well as the chosen approach for the modification of a HORIBA SPCS system leading to the PEMs4Nano laboratory system subsequently called **"PEMs4Nano LabSystem"**. This system consequently will be available for the upcoming emissions measurements at the project partners test benches.

The first step of enabling a PMP instrument for a detection efficiency to particles smaller than 23 nm will be using a CPC with a smaller D_{50} cut-off characteristic. The sensor used in the PEMs4Nano LabSystem will be the TSI CPC100 which was first modified for significantly increased detection efficiency down to 10 nm and then calibrated by TSI in the PEMs4Nano deliverable D2.02 ($\eta_{CPC100}(10 \text{ nm}) = 72,8\%$). However, the following additional factors must be taken into account for the overall PMP system considering sub-23 nm measurements:

- In the PMPs scope of solid-particle-counting only, the methodology primarily is relying on evaporative removal of any volatile nucleation particle mode which will be present in the size range below 23 nm, as well as the prevention of any (re-)occurrence of such a mode during aerosol conditioning and dilution in the VPR. However, in the case of a possible remainder of volatile particles in the nucleation mode leading to a volatile artifact during measurement which easily can exceed the concentration of solid particles the original PMP CPC D₅₀ characteristic deliberately was chosen to be at 23 nm, leading to a secondary neglection by non-detection of these artifacts.
- Due to the change to a 10 nm CPC characteristic, this secondary security is given up and the CPC will also detect any artificial volatile mode. Therefore, the robustness of the VPR unit against any volatile artifact needs to be increased. The standard PMP ET only evaporates volatile components, thus retaining the risk of their later re-nucleation. To prevent this more securely, the chosen solution for the PEMs4Nano LabSystem is to use a hot Catalytic Stripper (CS) which will remove volatile components by oxidation on a catalytic coated substrate, with evaporated components diffusing faster to the surface than the less-mobile particles.
- Moreover, with relevant particle loss mechanisms (diffusion, thermophoresis) becoming more prominent going to smaller particle sizes, overall PNCS small particle penetration needs to be optimized. As the heated catalytic stripper is cause to a big fraction of particle losses, a CS with low losses will be used and special effort should be put into optimizations of this component.

Both the modification of the CPC installed in the SPCS, as well as the modification by replacing the ET to a CS were performed on the premise of maintaining best consistency and interchangeability with current 23 nm SPCS systems under hardware and calibration aspects. Additionally, the goal was to be able to supply the project partners experiments with this first 10 nm laboratory instrument which is well proven and reliable compared to a long-term complete system redesign. As following results will show, these modifications lead to a system that is still fully compatible to original PMP VPR-specifications, as well as being able to measure particles starting at the 10 nm size range (results in section 5).



PEMs4Nano LabSystem - Modification of CPC

The internally installed original 23 nm CPC was replaced by the 10 nm CPC of D2.04 for the PEMs4Nano LabSystem, maintaining physical and electrical interfaces. The CPC k-factor calibrated in D2.04 was programmed into the SPCS configuration.

As the SPCS concept allows the connection of a second CPC in parallel using the "CPC AUX in" port, the original CPC100 calibrated to 23 nm will be available for simultaneous measurement of 10 nm and 23 nm channels during engine tests. This allows an estimation of changes in particle size distribution regarding 10 nm/23 nm ratios as well as identification of volatile artifacts or a solid nucleation mode in case of sole detection by the 10 nm CPC.

PEMs4Nano LabSystem - Modification of Evaporation Tube → Catalytic Stripper

In original HORIBA 23 nm SPCS systems, the evaporation tube is realized by an ET-module connecting the heated PND1 diluter with the cooling PND2 diluter. This ET-module itself consist of a 8 mm/10 mm (I.D./O.D.) tube with heating capable of creating temperatures up to 400°C. It is thermally isolated and double-bent to reach the respective connection ports in SPCS.

With the mentioned approach of possible module interchangeability, the PEMs4Nano LabSystem uses a CS-module that was designed to fit the same outer dimensions and connections as the original ET-module. The used module itself is shown on the left picture of Figure 2-4, and its installation in the PEMs4Nano LabSystem on the right picture. The module consists of a customized catalytic core supplied by *Catalytic Instruments* with an internal 220V heating of the core segment (see Figure 2-3). An additional bent stainless-steel tubing as well as an effective overall thermal insulation was designed to achieve the necessary dimensions for SPCS installation. The CS-module in the PEMs4Nano LabSystem will standardly be controlled to a temperature of 350°C, identical to typical ET-module temperatures. However, the heaters and thermal insulation is designed also to investigate higher temperatures up to 400°C and above.



Figure 2-3: Schematic of a CS catalytic core.

The CS-module used for the PEMs4Nano LabSystem was designed for a nominal flow of 2 lpm. Exceeding the standard 1 lpm in standard SPCS operation, this dimensioning thus maintains secure margins for a full removal of all volatile components even under severe engine operation conditions (e.g. cold-start, fuel enrichment, raw-exhaust without EAT, ...). Moreover, this layout provides margins for extended experiments which might be necessary for basic experiments on sub-23 nm measurements on the PEMs4Nano LabSystem with operation conditions outside SPCS standard settings like increased VPR flows, increased dilution margins and operation with multiple CPCs (though corresponding PCRF values will be necessary then).





Figure 2-4: Left picture: Heated & insulated catalytic stripper (CS) module used for the modification of the PEMs4Nano LabSystem - with identical outer dimensions of a standard HORIBA SPCS evaporation tube (ET) module. Right picture: Inlet of CS-module installed at outlet of the heated section of the PEMs4Nano LabSystem PND1 (insulation opened during installation).

However, considering particle losses of a CS, a trade-off between volatile component removal efficiency and (diffusional- and thermophoretic-) particle losses always has to be regarded. The PEMs4nano project partner at the University of Cambridge (UCAM, Boies group) thus has started investigations in parallel in 2018 to analyze particle losses and removal efficiency as well as methods for optimizing the overall CS-tradeoff. This will result in a further optimized CS-module with lower particle losses but sufficient volatile removal which will be used in the PEMs4Nano PEMS-system becoming available by deliverable D2.07 (October 2018). Moreover, due to the modularity of the PEMs4Nano LabSystem ET-module presented here, a feedback of these UCAM-results can be considered later for an optimized module for the PEMs4Nano LabSystem.



Figure 2-5: Finalized, fully modified PEMs4Nano LabSystem in testbed-operation (equipped to a double CPC setup).

The PEMs4Nano LabSystem after having been prepared for calibration- and engine-test measurements is shown in Figure 2-5. The established methodology of the PEMs4Nano LabSystem calibration will be presented in the following section 3, with results discussed in chapter 4. The whole procedure now easily can be repeated after realizing any further modification.



3 Experimental Setups

3.1 Overview of HORIBA PNCS calibration

During initial quality check as well as during annual maintenance, most HORIBA SPCS 2x00 systems in the European market undergo a PNCS calibration or validation performed by the HORIBA facility located in Oberursel, Germany.

Here, considering PMP calibration requirements previously described in chapter 2.4, PCRF calibration is performed on-site and the practical approach will be described in the following section 3.2. Moreover, the CPC-calibration either can be performed on-site at the HORIBA CPC-calibration testbed or by the TSI facility in Aachen (a short summary of the practical approaches for 10 nm CPC calibration already were described in deliverable D2.02).

Though not all worldwide located HORIBA facilities have the capability to also calibrate CPCs (thus will use a TSI facility for this service), the following described PCRF-calibration scheme is standardized for all HORIBA facilities.

3.2 HORIBA VPR PCRF calibration/validation

In the following sections, the specific procedure of PCRF calibration performed by HORIBA for SPCS-2x000 calibration will be described and explained in detail. In the last section 3.2.5, impacts and possible improvements for PCRF calibration of sub-23 nm systems will be discussed.

3.2.1 HORIBA PCRF calibration setup

In Figure 3-1, a schematic overview of the PCRF calibration setup used in the HORIBA facilities for SPCS 2x00 calibration is given. Model aerosol particles are generated using a NaCl particle generator and subsequently sizeclassified by a classifier & differential mobility analyzer (DMA) to particle sizes demanded by the respective calibration procedure – whereas the rest of the generated aerosol flow not fed into the DMA is dismissed into an exhaust duct. After leaving the DMA, the now 'monodisperse' particles either are fed directly to the SPCS's VPR outlet (dashed route) with a reference ultrafine-CPC (UFCPC) connected instead of the instruments 23 nm CPC100 in one calibration step. In the other calibration step, the classified particles are fed to the SPCS's inlet (dotted route) and diluted as well as conditioned by the SPCS's PMP VPR before being counted by the same UFCPC. Now, the ratio of particle counts measured at both locations are indicating the particle dilution & losses in the VPR.



Figure 3-1: Schematic of HORIBA VPR PCRF calibration setup

In the following passages, the main components used in this setup will be introduced briefly.



NaCl particle generator (LCU)

The particles used for PCRF calibration are generated by an HORIBA LCU (linearity check unit) system. This system internally uses a TSI model 3076 constant output atomizer. Here, compressed air introduced into the atomizer expands though a nozzle, forming a high-velocity jet. This jet produces an under-pressure which draws a NaCl-water-solution fed into the system and the jet subsequently atomizes the fluid. After immediately removing large droplets by impaction, the spray exiting the TSI 3076 is further conditioned in the LCU by feeding it through a heated tube (T > 100°C), a drain pot, a silica gel dryer and a second heated tube to evaporate the water content of the produced droplets and remove water vapor out of the aerosol stream. The resulting particles thus are mere solid NaCl particles in a dried air atmosphere. For further decrease of the produced particle concentration, additional dilution stages are provided in the LCU unit.

The concentration and the average particle size of the polydisperse particle size distribution produced by the LCU unit initially can be influenced by the amount of NaCl solved in ultrapure water fed into the atomizer. Here, a trade-off of small particle size versus sufficient particle concentration has to be chosen. The resulting typical particle sizes & concentrations, as well as the high concentration stability over 20 minutes are shown in the following Figure 3-2. The standard deviations of absolute concentrations over time, normalized to the respective averages are in the range of 1 %.



Figure 3-2: HORIBA PCRF calibration setup: High temporal stability of LCU aerosol particle concentration for the different used size settings of the classifier.

Classifier & DMA

The electrostatic particle size classifier used is a TSI 3080 with a TSI 3081 "Long-DMA" attached. Used flowrates are 15,0 Slpm for sheath flow in Dual-Blower mode and 1,5 Slpm for aerosol flow rate, resulting in a sheath/aerosol factor of 10:1 which is recommended by TSI for optimal size classification (small width of output "quasi-monodisperse" size distribution in terms of geometric standard deviation, but sufficient overall particle number penetration at the same time).

The aerosol flow rate through the classifier system is drawn by the subsequently connected components, i.e. the reference UFCPC directly, or the SPCS VPR (with additional bypass line), but measured by the TSI classifier system itself using a flow-orifice meter and differential pressure measurement. Where the sole UFCPC is already creating the desired 1,5 Slpm flow when directly connected to the DMA during measurement of the undiluted



concentration, the SPCS VPR inlet flow is lower (~0,1-0,44 Nlpm) and is thus added up by an additional bypass line an overall 1,5 Slpm during the calibration of the diluted concentration post VPR (adjusted by a needle valve connected to vacuum).

Reference-CPC (UFCPC, REF)

A TSI 3776 ultrafine-CPC (UF-CPC) with a lower particle detection size limit of 2.5 nm is used as a reference counter (REF) during PCRF calibration.

The advantage of using an UFCPC for these calibration purposes is its high particle counting efficiency even going to small particle sizes, resulting in higher effective particle counts during PCRF calibration on high dilution settings with small particles – and thus providing more reliable results. The UFCPC's sensitivity to small particles is achieved by several internal design measures, where the most noteworthy is the use of a particle-free sheath flow to reduce internal particle losses. This flow is created by splitting and filtering a part of the incoming aerosol flow. Where this internal flow-splitting generally is affecting the CPC's overall counting accuracy due necessary knowledge of splitting accuracy & stability, any errors in this splitting factor can be ignored by HORIBA PCRF calibration methodology as these splitting errors will be completely cancelled out in the PCRF ratio assuming them being a constant factor over one calibration point (see following considerations in section 3.2.3).

HORIBA SPCS2x00 (DUT)

Regarding the HORIBA SPCS2x00 to be PCRF-calibrated / -validated using this setup, its original CPC (CPC100) will be removed and calibrated separately regarding PMP demands. In lieu of, the PCRF calibration-setups reference UFCPC then is connected to the SPCS's VPR CPC output. Then, the SPCS internal flow calibration procedure ("CPC/CFO calibration") is initiated to adjust the SPCS diluters to the increased inlet flow of the UFCPC (1, SIpm instead of 1,0 SIpm for a CPC100).

For the alternating attachment of the calibration aerosol exiting the DMA during PCRF calibration, HORIBA SPCS2x00 systems have designated, externally accessible ports. The calibration aerosol is either being connected to the VPR inlet ("VPR AUX IN") or to the VPR outlet ("CPC AUX in") directly leading to the (reference-)CPC, as depicted in Figure 3-1. Instrument control, data acquisition, the calibration automatic sequence control as well as the calculation of the new PCRF-factors all is implemented in the respective HORIBA SPCS software. A detailed explanation of calibration procedure and its single steps will follow in section 3.2.2.

Calibration of instruments

The Classifier and UFCPC used during calibration are maintained and calibrated on a yearly basis directly by the instrument manufacturer TSI.

Moreover, absolute accuracy effectively is mainly relevant considering the size value of classified particles, whereas other inaccuracies can be cancelled out, also assuming them being constant and cancelled out over one calibration point (also refer to following considerations in section 3.2.3).

3.2.2 HORIBA PCRF calibration procedure / sequence

Regarding the PMP PCRF-equation (Eq. 2-2), particle penetration factors will calculate as follows, considering each preset dilution setting $Dil_{SPCS,i}$ of the SPCS.

$$PCRF(D_P, Dil_{SPCS,i}) = \frac{c_{UFCPC,in}(D_P)}{c_{UFCPC,out}(D_P, Dil_{SPCS,i})}.$$
(Eq. 3-1)

Dilution settings $Dil_{SPCS,i}$ available in HORIBA SPCS 2x000 systems are summarized in Table 3-1. Intermediate dilution factors are possible in principle – but should not be used as PCRF calibration factors are only available for these preset dilution settings.



Dilution setting i	Dilution 1 (PND1)	Dilution 2 (PND2)	Dil _{SPCS,i}	Overall Dilution without DSU (PND1xPND2):	Overall Dilution with DSU (10xPND1xPND2)
i = 1	10	15	$Dil_{SPCS,1} =$	150	1 500
i = 2	20	15	$Dil_{SPCS,2} =$	300	3 000
i = 3	50	15	$Dil_{SPCS,3} =$	750	7 500
i = 4	100	15	$Dil_{SPCS,4} =$	1 500	15 000
i = 5	200	15	$Dil_{SPCS,5} =$	3 000	30 000

Table 3-1: Preset dilution settings (*Dil*_{SPCS.i}) available in HORIBA SPCS 2x00 systems

Regarding the PCRF calibration of one dilution setting $Dil_{SPCS,i}$, the procedure will be as following for each particle size D_P to be measured: $D_P = [100nm, 50nm, 30nm]$ for standard PMP calibration, $D_P = [100nm, 50nm, 30nm, 23nm, 15nm, 10nm]$ for sub-23 nm investigations. Each step first will be stabilized for 60 - 120 s and subsequently averaged during 120 s:

- Step1: Connect DMA output to SPCS VPR output ("CPC AUX IN"), determination of undiluted concentration $c_{\text{UFCPC,in,step1}}(D_{\text{P}})$ by UFCPC (this is the VPR inlet concentration in Step2 considering LCU stability).
- Step2: Connect DMA output to SPCS VPR input ("VPR AUX IN"), determination of diluted concentration $c_{\text{UFCPC,out,step2}}(D_{\text{P}}, Dil_{\text{SPCS},i})$ (VPR outlet conc.) using dilution setting $Dil_{\text{SPCS},i}$.
- Step3: Connect DMA output to SPCS VPR output ("CPC AUX IN"), 2nd determination of undiluted concentration c_{UFCPC,in,step3}(D_P) (repetition measurement of VPR inlet concentration).

Now, with additional consideration of averaging inlet measurements of step 1 and step 3, we arrive at the final formula for one $PCRF(D_P, Dil_{SPCS,i})$ in the HORIBA's PCRF calibration process:

$$PCRF\left(D_{P}, Dil_{SPCS,i}\right) = \frac{\frac{1}{2}\left(c_{UFCPC,in,step1}(D_{P}) + c_{UFCPC,in,step3}(D_{P})\right)}{c_{UFCPC,out,step2}\left(D_{P}, Dil_{SPCS,i}\right)}.$$
(Eq. 3-2)

Regarding the automated sequence of determining the PCRF for all dilution settings, inlet-concentrations $c_{\text{UFCPC,in,stepX}}$ only are determined at the start and at the end of every D_{P} setting with all dilution settings $Dil_{\text{SPCS},i}$ sequentially measured in-between. This optimization in test-time is allowed due to the high temporal stability of the LCU particle generator. The sequence thus determines the following average values:

- 1. $c_{\text{UFCPC,in,step1}}(D_{\text{P}})$
- 2. $c_{\text{UFCPC,out,step2}}(D_{\text{P}}, Dil_{\text{SPCS},1} = 100) \rightarrow c_{\text{UFCPC,out,step2}}(D_{\text{P}}, Dil_{\text{SPCS},2} = 300) \rightarrow c_{\text{UFCPC,out,step2}}(D_{\text{P}}, Dil_{\text{SPCS},3} = 750) \rightarrow c_{\text{UFCPC,out,step2}}(D_{\text{P}}, Dil_{\text{SPCS},4} = 1500) \rightarrow c_{\text{UFCPC,out,step2}}(D_{\text{P}}, Dil_{\text{SPCS},4} = 3000)$
- 3. $c_{UFCPC,in,step3}(D_P)$

After repeating this sequence for all particle size values D_P to be calibrated, HORIBA SPCS software now calculates the respective average $\overline{PCRF}(Dil_{SPCS,i})$ values for every preset dilution setting $Dil_{SPCS,i}$. For standard PMP calibration, $D_P = [100nm, 50nm, 30nm]$, this develops to the equation:

$$\overline{PCRF}(Dil_{SPCS,i}) = \frac{PCRF(30nm, Dil_{SPCS,i}) + PCRF(50nm, Dil_{SPCS,i}) + PCRF(100nm, Dil_{SPCS,i})}{3}.$$
 (Eq. 3-3)



An example result dataset of a standard PMP PCRF calibration results of a HORIBA SPCS-2100 system is given in Table 3-2, also showing the very high stability of LCU particle generation ("LCU Stability Error").

			Step 1	Step 2	Step 3			
PND 1	PND 2	Particle Size	Inlet Conc. #1 (#/cm ³)	Outlet Conc. (#/cm ³)	Re-Inlet Conc. #2 (#/cm ³)	LCU Stability Error	PCRF fr(d)	ratio*
10	15	30	46897,3	271,3	48478,2	3,37%	172,88	1,04
10	15	50	53306,1	296,6	53214,4	-0,17%	179,71	1,08
10	15	100	54186,1	326,3	53301,3	-1,63%	166,07	
20	15	30	46897,3	140,2	48478,2	3,37%	334,51	0,98
20	15	50	53306,1	150,7	53214,4	-0,17%	353,79	1,04
20	15	100	54186,1	158,9	53301,3	-1,63%	341,04	
50	15	30	46897,3	55,4	48478,2	3,37%	846,05	1,02
50	15	50	53306,1	63,4	53214,4	-0,17%	840,74	1,02
50	15	100	54186,1	65,5	53301,3	-1,63%	827,60	
100	15	30	46897,3	26,1	48478,2	3,37%	1795,70	1,08
100	15	50	53306,1	31,2	53214,4	-0,17%	1708,96	1,03
100	15	100	54186,1	32,7	53301,3	-1,63%	1656,16	
200	15	30	46897,3	13,6	48478,2	3,37%	3449,74	1,08
200	15	50	53306,1	16,7	53214,4	-0,17%	3196,46	1,00
200	15	100	54186,1	16,9	53301,3	-1,63%	3206,10	

Table 3-2 Example result dataset of SPCS PCRF calibration (HOR calibration of LabSystem before modification).

The given LCU stability error in Table 3-2 is the drift in concentration from measurement of undiluted classified aerosol between Step 1 and Step3 – with measurement of all dilution steps for one particle size in between during Step 2. The ratio-value indicates the respective PCRF-value normalized to the PCRF at 100 nm.

3.2.3 Consideration & cancellation of particle loss effects during PCRF calibration

As the determination of the \overline{PCRF} factor described in section 2.4.1 should only include dilution and particle losses occurring in the VPR on the way from PNCS inlet to CPC inlet, thorough considerations of parasitic particle losses on additional lines used for particle transfer during calibration should be carried out, and losses should be neutralized (e.g. by symmetric lines) or avoided as far as possible. Doing this, Table 3-3 depicts and summarizes elements of particle losses to be considered during \overline{PCRF} calibration (also compare with grey labels in Figure 3-1).

Table 3-3 Elements / components of particle penetration factors to be considered during PCRF calibration.

Variable	Description
$c_{\mathrm{DMA,out}}(D_{\mathrm{P}})$	Size-dependent particle concentration at outlet of DMA. $D_{\rm P}$'s used are 100nm, 50nm, 30nm for conventional <i>PCRF</i> determination as well as additional setting of 15nm and 10nm for Sub-23nm investigations.
$\eta_{\mathrm{DMA} \to \mathrm{SPCS}}(D_{\mathrm{P}})$	Particle losses of the tubing between DMA and SPCS (same tubing for $N_{\rm in}(D_{\rm P})$ and $N_{\rm out}(D_{\rm P})$, dashed or dotted line).
Dil _{SPCS,i}	Dilution factor of SPCS VPR's dilution setting <i>i</i> (gaseous dilution).
$\eta_{\text{SPCS,VPR}}(D_{\text{P}}, Dil_{\text{SPCS},i})$	Particle losses in SPCS's VPR during VPR's dilution setting i.
$\eta_{\mathrm{SPCS} o \mathrm{UFCPC}}(D_{\mathrm{P}})$	Particle losses of the tubing between SPCS and UFCPC (dashed-dotted-line).



$\eta_{\mathrm{UFCPC}}(D_{\mathrm{P}})$	Particle counting efficiency of UFCPC (including accuracy of UFCPC's internal flow splitting).			
$c_{\rm UFCPC}(D_{\rm P})$	Particle concentration reading of UFCPC			
$c_{\mathrm{UFCPC,in}}(D_{\mathrm{P}})$	- inlet particle concentration reading before VPR (see step 1 and step 3)			
$c_{\mathrm{UFCPC,out}}(D_{\mathrm{P}})$	- outlet particle concentration reading after VPR (see step 2)			
$c_{\text{UFCPC,[in,out],stepX}}(D_{\text{P}})$	 particle concentration reading during stepX = [step1, step2, step3]. 			

Now, developing the original PMP PCRF-equation (Eq. 2-2) regarding the practical HORIBA setup of Figure 3-1 and particle penetration factors of Table 3-3, this evolves into:

$$PCRF(D_P, Dil_{SPCS,i}) = \frac{N_{in}(D_P)}{N_{out}(D_P, Dil_{SPCS,i})} =$$

$$=\frac{c_{DMA,out}(D_P)\eta_{DMA\to SPCS}(D_P)\eta_{SPCS\to UFCPC}(D_P)\eta_{UFCPC}(D_P)}{c_{DMA,out}(D_P)\eta_{DMA\to SPCS}(D_P)\frac{1}{Dil_{SPCS,i}}\eta_{SPCS,VPR}(D_P,Dil_{SPCS,i})\eta_{SPCS\to UFCPC}(D_P)\eta_{UFCPC}(D_P)}=$$

$$= \frac{c_{DMA,out}(D_{P}) \eta_{DMA \to SPCS}(D_{P}) \eta_{SPCS \to UFCPC}(D_{P}) \eta_{UFCPC}(D_{P})}{c_{DMA,out}(D_{P}) \eta_{DMA \to SPCS}(D_{P}) \frac{1}{Dil_{SPCS,i}} \eta_{SPCS,VPR} (D_{P}, Dil_{SPCS,i}) \eta_{SPCS \to UFCPC}(D_{P}) \eta_{UFCPC}(D_{P})}$$
(Eq. 3-4)

$$= Dil_{SPCS,i} * \eta_{SPCS,VPR} \left(D_P, Dil_{SPCS,i} \right) = \frac{c_{UFCPC,in}(D_P)}{c_{UFCPC,out}(D_P, Dil_{SPCS,i})}.$$

Here, cancellation of equivalent inlet-concentrations was performed under these assumptions:

- Temporal stability of the LCU aerosol generators particle output during PCRF determination. (This is practically checked by determining $N_{in}(D_P)$ as step 1 & 3 before and after $N_{out}(D_P)$ in step 2. Specified tolerable drift is < 5%. Constant drift effects are furthermore cancelled out by using average value of step 1 and step 3 as shown in following equation (Eq. 3-6).)
- Stable DMA particle size classification.
 (Can be assumed whilst maintaining constant DMA flows.)
- Equivalent particle penetration factors. (Regarding the usage of the same particle transfer tubing for step 1&3 and step 2.)

Consequently, Formula (Eq. 3-4) now results in:

$$PCRF\left(D_{P}, Dil_{SPCS,i}\right) = \frac{N_{in}(D_{P})}{N_{out}(D_{P})} = Dil_{SPCS,i} * \eta_{SPCS,VPR}\left(D_{P}, Dil_{SPCS,i}\right) = \frac{c_{UFCPC,in}(D_{P})}{c_{UFCPC,out}\left(D_{P}, Dil_{SPCS,i}\right)} \cdot$$
(Eq. 3-5)

It can now easily be seen that all listed parasitic influences are now perfectly cancelled out and that the ratio of UFCPC-counts $\left(\frac{c_{\text{UFCPC,in}}(D_{\text{P}})}{c_{\text{UFCPC,out}}(D_{\text{P}})}\right)$ directly represents the mere particle count reduction factor intended and defined by PMP, only including dilution $(Dil_{\text{SPCS},i})$ and only including particle penetration / losses occurring inside the PNCS's / SPCS's VPR $(\eta_{\text{SPCS,VPR}} (D_{\text{P}}, Dil_{\text{SPCS},i}))$.



And, with additional consideration of averaging step 1 and step 3, we arrive at the final formula used during HORIBA's PCRF calibration process:

$$PCRF\left(D_{P}, Dil_{SPCS,i}\right) = \frac{\frac{1}{2}\left(c_{UFCPC,in,step1}(D_{P}) + c_{UFCPC,in,step3}(D_{P})\right)}{c_{UFCPC,out,step2}(D_{P}, , Dil_{SPCS,i})}.$$
(Eq. 3-6)

3.2.4 Extension of *PCRF*-definition including small particle sizes.

Analogous to Equation (Eq. 2-3), the \overline{PCRF} -average calibration values will be calculated as average of the different size setpoints PCRF (D_P)'s. Complementary to the PCRF definition of PMP using 100 nm, 50 nm and 30 nm values, two more average PCRF definitions will be used in this report, also including 15 nm ((Eq. 3-8) & (Eq. 3-9)) and/or 23 nm values, (Eq. 3-8):

$$\overline{PCRF} = \overline{PCRF_{30-100}} = \frac{PCRF(30nm) + PCRF(50nm) + PCRF(100nm)}{3}$$
(Eq. 3-7)

$$\overline{PCRF_{23-100}} = \frac{PCRF(23nm) + PCRF(30nm) + PCRF(50nm) + PCRF(100nm)}{4}$$
(Eq. 3-8)

$$\frac{PCRF_{15-100}}{5} = \frac{PCRF(15nm) + PCRF(23nm) + PCRF(30nm) + PCRF(50nm) + PCRF(100nm)}{5}$$
(Eq. 3-9)

The expression $\overline{PCRF_{xx-100}}$ will subsequently be used as a variable designation for these three definitions. As the exact embodiment of any future PN regulation including Sub-23 nm particles cannot be foreseen yet, all three definitions will be used in the following to allow further investigations of qualitative influence using different PCRF-definitions. An inclusion of an additional 10 nm value has not been followed in the current investigations, both due to disproportionally increasing complexity of the calibration setup and proceeding as well as to prevent a disproportionately high influence of small particle losses in the overall $\overline{PCRF_{xx-100}}$ factor. For a final definition, it should be suggested that PCRF sizes should deliberately weighted considering emitted size distributions of currently prevailing modern engine concepts and respective influence weighted by the overall PNCS size dependent efficiency.

3.2.5 Further considerations on PCRF methodology and possible improvements

LCU particle morphology (influence on counting efficiency)

It is well known that CPC may exhibit different size dependent cut-off efficiency curves when challenged with different calibration aerosol. This is caused by effects of particle morphology and surface composition influencing the condensation- and growth-process in the CPC condenser.

During the HORIBA PCRF calibration however – and contrary to any absolute calibration like a CPC-calibration comparing to an electrometer as an absolute reference instrument – particle morphology should not have any appreciable influence due to the relative design of the HORIBA PCRF methodology:

This is because any material-based influence on particle counting efficiency $\eta_{\rm UFCPC}(D_{\rm P})$ of the reference UFCPC caused by particle morphology will be canceled out after relative calculation of $N_{\rm in}(D_{\rm P}) / N_{\rm out}(D_{\rm P})$, with the influence physically being the same for both VPR inlet and VPR outlet measurements. Consequently, comparable



PCRF results are expected using any fully-solid calibration aerosol material like e.g. NaCl, soot-like Cast or graphite-spark particles (while neglecting or taking care of secondary influences of particle charge in size classification etc.).

LCU size distribution (influence on size classification & double charges)

However, the current LCU size distribution is not fully optimal for < 23 nm calibration due to the existence of a fraction of double charged particles becoming greater below the generated size distributions mean diameter (approx. 40 nm). However – and contrary to above mentioned CPC calibration against a FCAE – these double charges have no direct influence during detection with an CPC reference – both due to the insensitivity of CPCs to particle charge as well as the relative measurements of inlet- and outlet concentrations by the same instrument.

However, a remaining influence is in terms of 'real' average particle size exciting the DMA, with the average being slightly increased due to larger double-charged particles exhibiting the same electrical mobility as the originally desired particle size. However, this influence will be neglected in the following experiments due to the following reasons:

- Reducing this influence can be achieved by changing NaCl concentration (but limited possibility to achieve very small size distributions with sufficient concentration at the same time) or by replacing the kind of particle generator. However, the first goal will be maintaining a similar setup for both standard 23 nm and Sub-23 nm calibration at HORIBA's calibration facility as well as keeping calibration effort in an acceptable range by avoiding the necessity to maintain, change and stabilize different solutions. Thus, this approach will not be followed here in the first place but might be analyzed in the future: Here, a unification of calibration aerosol for CPC-, Lab-system- and PEMS-system-calibration (e.g. HORIBA OBS-PN) might be possible using soot-like cast-aerosol.
- The 'real' average particle size leaving the DMA is slightly larger than the size adjusted, containing larger double-charged particles. However, whilst maintaining the same input particle size distribution (same concentration of NaCl-solution), this "offset" will be rather constant while maintaining the current HORIBA calibration methodology and thus inter-comparability of HORIBA results is given.

Nonetheless, this should be small due to the small probability of double charges for these small particles. It will be point of further investigation, quantification and optimization if necessary – also in regard of the precise embodiment of any future particle number counting regulation including counting and calibration provisions for Sub-23 nm setups. This should then additionally allow better comparability with (PCRF-)calibration results achieved by other laboratories or instrument manufacturers.



3.3 DSU PCRF calibration/validation

Whilst non-specified in original PMP, adding DSU raw-exhaust pre-dilution poses an additional component for particle losses during sample transfer from the exhaust line to the CPC and is thus also calibrated by HORIBA, based on the same basic principles as the previously described PCRF calibration methodology. Beside dilution and particle losses induced by the DSU itself, also losses occurring in the PTT tubing are included in this methodology.

Comparing this DSU raw-exhaust dilution including the appliance of such an DSU-PCRF (\overline{PCRF}_{DSU}) on one side with certification PN-measurements using CVS-/PFDS-exhaust dilution on the other side, it is obvious that in the latter cases no PCRF is defined and only dilution factors will find their way into final calculation of PN emission values – being one factor to be considered when comparing certification- with raw-PN-measurements.

3.3.1 HORIBA DSU calibration setup

As illustrated in the following Figure 3-3, DSU calibration is using the exact same calibration aerosol supply consisting of the LCU NaCl particle generation unit as well as the UFCPC as reference CPC.

For DSU calibration, the monodisperse aerosol leaving the DMA is either directly fed to the UFCPC in the 1st and 3rd calibration step for measurement of the undiluted aerosol inlet concentration, or it is fed to the DSU inlet in the 2nd calibration step and consequently diluted and transferred though the PTT before being measured by the UFCPC.



Figure 3-3: Schematic of HORIBA DSU PCRF calibration setup

The exact same tubing to the UFCPC is used connecting during $1^{st}/3^{rd}$ step via the dashed route to the dotteddashed tube combing from the DMA outlet. During 2^{nd} step, the dotted-dashed line is connecting to the DSU inlet port and the dotted route after the PTT to the UFCPC inlet port.



3.3.2 HORIBA DSU calibration procedure / sequence

Similar to section 3.2.3, DSU+PTT particle penetration factors will calculate as followed.

$$PCRF_{DSU}(D_P) = \frac{c_{UFCPC,in}(D_P)}{c_{UFCPC,out}(D_P)}.$$
(Eq. 3-10)

As the DSU dilution factor is a constant 1:10, the procedure will be only performed once for each particle size D_P to be measured ($D_P = [100nm, 50nm, 30nm]$ like in standard PMP calibration, $D_P = [100nm, 50nm, 30nm, 23nm, 15nm, 10nm]$ for Sub-23 nm investigations). Each step first will be stabilized for 120 s and subsequently averaged during 120 s.

- Step 1: Connect DMA output to tubing going to UFCPC ($\eta_{\text{DMA}\rightarrow\text{DSU}} \rightarrow \eta_{\text{DSU}\rightarrow\text{UFCPC}}$), Determination of DSU inlet concentration $c_{\text{UFCPC.in.step1}}(D_{\text{P}})$
- Step 2: Connect DMA output to DSU input $(\eta_{\text{DMA}\rightarrow\text{DSU}} \rightarrow \text{DSU inlet} \rightarrow \text{PTT} \rightarrow \eta_{\text{DSU}\rightarrow\text{UFCPC}})$, Determination of DSU inlet concentration $c_{\text{UFCPC,out,step2}}(D_{\text{P}})$
- Step 3: Reconnect DMA output to tubing going to UFCPC ($\eta_{\text{DMA}\rightarrow\text{DSU}} \rightarrow \eta_{\text{DSU}\rightarrow\text{UFCPC}}$), Determination of DSU inlet concentration $c_{\text{UFCPC,in,step1}}(D_P)$

Now, with additional consideration of averaging inlet measurements of step 1 and step 3, we arrive at the final formula for the DSU's *PCRF* (D_P , $Dil_{SPCS,i}$) used during HORIBA's PCRF calibration process:

$$PCRF_{DSU}(D_P) = \frac{1/2 \left(c_{UFCPC,in,step1}(D_P) + c_{UFCPC,in,step3}(D_P) \right)}{c_{UFCPC,out,step2}(D_P)}.$$
(Eq. 3-11)

After repeating this sequence for all particle size values D_P to be calibrated, HORIBA SPCS software now calculates the respective \overline{PCRF}_{DSU} , or standard PMP-like calibration, $D_P = [100 \text{ nm}, 50 \text{ nm}, 30 \text{ nm}]$:

$$\overline{PCRF}_{DSU} = \frac{PCRF(30nm) + PCRF(50nm) + PCRF(100nm)}{3}.$$
(Eq. 3-12)

Additional definitions including 15 nm and/or 23 nm losses in the DSU will be used equivalent to equations (Eq. 3-8) and (Eq. 3-9).

3.3.3 Consideration & cancellation of particle loss effects during DSU calibration

Similar as done for HORIBA PCRF methodology, parasitic particle losses on additional lines used for particle transfer during calibration can be largely neutralized (e.g. by symmetric lines) or avoided as far as possible. Doing this, Table 3-4 depicts and summarizes elements of particle losses to be considered during DSU calibration (also compare with grey labels in Figure 3-3).



Table 3-4: Elements of particle penetration factors to be considered during DSU calibration.

Variable	Description
$c_{\mathrm{DMA,out}}(D_{\mathrm{P}})$	Size-dependent particle concentration at outlet of DMA. $D_{\rm P}$'s used are 100nm, 50nm, 30nm for conventional <i>PCRF</i> determination as well as additional setting of 15nm and 10nm for Sub-23nm investigations.
$\eta_{\mathrm{DMA} o \mathrm{DSU}}(D_{\mathrm{P}})$	Particle losses of the tubing between DMA and DSU (same tubing for $N_{in}(D_P)$ and $N_{out}(D_P)$, see dashed-dotted-line).
$Dil_{\rm DSU}=10$	Dilution factor of SPCS VPR's dilution setting i (gaseous dilution).
$\eta_{\mathrm{DSU}}(D_{\mathrm{P}})$	Particle losses in SPCS's VPR during VPR's dilution setting i.
$\eta_{\text{DSU} o \text{UFCPC}}(D_{\text{P}})$	Particle losses of the tubing between DSU / PTT outlet and UFCPC (see dotted or dashed lines).
$\eta_{\mathrm{UFCPC}}(D_{\mathrm{P}})$	Particle counting efficiency of UFCPC (including accuracy of UFCPC's internal flow splitting).
$c_{\rm UFCPC}(D_{\rm P})$	Particle concentration reading of UFCPC
$c_{\mathrm{UFCPC,in}}(D_{\mathrm{P}})$	- inlet particle concentration reading before DSU (see step 1 and step 3)
$c_{\mathrm{UFCPC,out}}(D_{\mathrm{P}})$	 outlet particle concentration reading after DSU & PTT (see step 2)
$c_{UFCPC,[in,out],stepX}(D_P)$	 particle concentration reading during stepX = [step1, step2, step3].

Now, regarding the practical HORIBA setup of Figure and particle penetration factors of Table 3-4, this the PCRF applied to DSU&PTT evolves into:

$$PCRF_{DSU}(D_P) = \frac{N_{in}(D_P)}{N_{out}(D_P)} =$$

$$= \frac{c_{DMA,out}(D_P) \eta_{DMA \to DSU}(D_P) \eta_{DSU \to UFCPC}(D_P) \eta_{UFCPC}(D_P)}{c_{DMA,out}(D_P) \eta_{DMA \to DSU}(D_P) \frac{1}{Dil_{DSU}} \eta_{DSU} (D_P) \eta_{DSU \to UFCPC}(D_P) \eta_{UFCPC}(D_P)} =$$

$$= \frac{c_{DMA,out}(D_P) \eta_{DMA \to DSU}(D_P) \eta_{DSU \to UFCPC}(D_P) \eta_{UFCPC}(D_P)}{c_{DMA,out}(D_P) \eta_{DMA \to DSU}(D_P) \frac{1}{Dil_{DSU}} \eta_{DSU} (D_P) \eta_{DSU \to UFCPC}(D_P) \eta_{UFCPC}(D_P)} =$$

$$= Dil_{DSU} * \eta_{DSU} (D_P) = \frac{c_{UFCPC,in}(D_P)}{c_{UFCPC,out}(D_P)}.$$
(Eq. 3-13)

Again, it is obvious that all listed parasitic influences are now perfectly cancelled out and that the ratio of UFCPCcounts $\left(\frac{c_{\text{UFCPC,in}}(D_{\text{P}})}{c_{\text{UFCPC,out}}(D_{\text{P}})}\right)$ directly represents the mere dilution Dil_{DSU} and particle losses imposed during exhaust sample transfer through DSU and PTT ($\eta_{\text{DSU}}(D_{\text{P}})$).



3.4 AVACS-setup for PEMs4Nano basic aerosol investigations

Besides the HORIBA SPCS calibration setup described in the preceding sections, an additional fully automated aerosol laboratory / test-bench has been used in basic PEMs4Nano aerosol investigations characterizing individual PNCS components. This setup is designated SPCS-AVACS (Automated Validation and Calibration System for HORIBA SPCS), it's basic flow schematic is shown in Figure 3-4.



Figure 3-4: Schematic of AVACS-setup for basic aerosol investigations – with exemplary external setup for the determination of component particle penetration.

In AVACS, model aerosol particles are prepared by following steps:

- Aerosol generation by Palas DNP 3000 graphite-spark particle generator
- 1st dilution stage (controlled)
- Classifier & DMA stage (controlled)
- 2nd dilution stage (controlled)
- Homogenous splitting to reference instrument (CPC 1) and (several) components or devices under test (DUT, CPC_i)
- Additional equipment available in AVACS allow the setup of additional controlled feed-up or bypass flows to achieve necessary flow rates or incremental flow-rate changes.

As the AVACS setup allows a very stable and fully automated processing of measurement-scans over particle sizes with a large set of controlled parameters as well as non-supervised repetitions of any test, and the possibility to include and control many different instruments in parallel, it can be easily used for the acquisition of large and precise aerosol measurement datasets and thus will be also used for these and future basic aerosol investigations in the PEMs4Nano project.



4 Basic aerosol investigations on components of PEMs4Nano LabSystem

4.1 Intercalibration of reference-CPCs

In order to be able to determine the precise particle penetration characteristic $\eta_X(D_P)$ of a component X, using the counting ratio of two different CPC-sensors pre- $(c_{CPC,1}(D_P))$ and post- $(c_{CPC,i}(D_P))$ the component to be investigated (compare Figure 3-4), exact ratios of the respective sensors response $\eta_{CPC,i}(D_P)$ have to be determined first to be able to eliminate their different size-dependent sensitivity as well as overall k-calibration:

$$\eta_X(D_P) = \frac{c_{CPC,i}(D_P)}{c_{CPC,1}(D_P)} / \frac{\eta_{CPC,i}(D_P)}{\eta_{CPC,1}(D_P)}.$$
(Eq. 4-1)

Even in the case of identically constructed CPCs, the ratio $\eta_{CPC,i}(D_P) / \eta_{CPC,1}(D_P)$ might slightly deviate from unity due to unavoidable differences in fabrication and calibration. For preparation of such penetration measurements, 7 different CPC listed in Table 4-1 (reference CPC 1 plus CPC_i with i=[2...7]) have been intercalibrated in parallel using the AVACS setup as shown in Figure 4-1.



Figure 4-1: AVACS setup for intercalibration of reference-CPCs

As CPC2 to CPC6 were CPC100 originally calibrated to a D_{50} of 23 nm, all respective condenser and saturator temperatures previously had been manually set to the temperatures of the CPC3772 10 nm counter CPC1 – to achieve best efficiency also going to small particles. As this notable change in CPC100-temperatures will also result in changing particle growth and thus deviating actual coincidence effects (compare (Eq. 2-1)) compared to the internally applied coincidence correction, a re-calculation and correction of coincidence effects to 10 nm coincidence correction factors was applied during post-processing of the measurement data.

Using this setup and methodology for all CPCs, 10 independent scans of $c_{CPC,i}(D_P)$ (each flow and coincidencecorrected) have been acquired with each scan consisting of 25 measurement points evenly distributed over the logarithmic D_P -scale from 10 nm to 160 nm. Using this data, subsequently all $\eta_{CPC,i}(D_P) / \eta_{CPC,1}(D_P)$ were calculated by (Eq. 4-1) using $\eta_X(D_P) = 1$ due to identical lines to each CPC_i. Figure 4-2 shows the resulting intercalibration curves averaged over all scans (with $\pm 1\sigma$ error bars applied). As instabilities in CPC2 were found during post-processing, its data will be excluded in the following. These resulting $\eta_{CPC,i}(D_P) / \eta_{CPC,1}(D_P)$ -factors will be used in succeeding investigations by default.



Table 4-1: List of CPCs used for basic investigations.

CPC-designation	CPC1	CPC2	СРСЗ	CPC4	CPC5	CPC6	CPC7
<i>i</i> =	1	2	3	4	5	6	7
СРС-Туре	CPC-3772	CPC-100	CPC-100	CPC-100	CPC-100	CPC-100	CPC-3772
Serial-Number	3772112701	C100150202	C100161302	C100160201	C100114403	C100164303	3772171102
K-Factor	(1,05)	1,0412	1,0829	1,0493	1,0873	1,0204	(1,05)
Original	30.0	28 5	28 5	285	385	38.8	30.0
T_Saturator [°C]	59,0	50,5	50,5	56,5	56,5	50,0	39,0
Original	21.0	30.0	30.7	30.8	30.8	30.8	22.0
T_Condensor [°C]	21,0	50,9	50,7	50,8	50,8	50,8	22,0
Original	40.0	40 0	40 0	40 0	40 0	40 0	40 0
T_Optics [°C]	40,0	40,0	40,0	40,0	40,0	40,0	40,0
Modified	39.0	39.0	39.0	39.0	39.0	39.0	39.0
T_Saturator [°C]	33,0	33,0	33,0	33,0	33,0	33,0	33,0
Modified	21.0	21.0	21.0	21.0	21.0	21.0	21.0
T_Condensor [°C]	21,0	21,0	21,0	21,0	21,0	21,0	21,0
Modified	40.0	40 0	40 0	40 0	40 0	40 0	40 0
T_Optics [°C]	-0,0	-0 ,0	-0 ,0	-0,0	0,0	-0 ,0	-0 ,0



Figure 4-2: Size-dependent intercalibration results of used CPCs (error-bars = $\pm \sigma$).

Regarding the intercalibration curves shown in Figure 4-2, it can be concluded:

 The distinctive flat plateau regions going to medium- and large particle sizes show the correct recalculation of coincidence factors as the model aerosol particle concentration (GMD~40nm) is largely changing in this region (leading to non-monotonously-increasing efficiency curves without re-calculation). Relative to CPC1, the level of the plateaus is distinctive to the CPC absolute calibration with its value being similar to the k-factor-ratios, despite slightly different definitions.



- In particular, the very small error bars at medium- and large particle sizes prove the very high stability of both the AVACS-setup as well of the investigated CPCs (average $\overline{\sigma} = 0,0016$ above 20 nm) over the 10 performed scans. The increased errors going to small particles are caused by a smaller model aerosol concentration and decreasing counting efficiencies of all CPC as well as influences of slight changes due to temperature control etc.
- Due to small deviations in final cut-off characteristics, either monotonously falling (smaller D₅₀) or increasing (larger D50) intercalibration-curves result going to small particle sizes. This is caused by minimal device-specific differences in temperature and tolerances. Cut-off curves with similar D₅₀ but deviating slope lead to slightly S-shaped intercalibration-curves at the respective cut-off intersection area.

Regarding the overall level of the CPCs plateaus, their arrangement moreover still is widely complying with the CPCs original k-factor calibration. However, the ratio's overall level also is determined by CPC1s arbitrary k-factor (as such a factor is not defined for a non-PMP CPC like the CPC3772). Though deviating from original calibration, the maintained arrangement may be caused by fabrication tolerances of the CPC CFO flows also incorporated by the k-factor calibration.

4.2 Catalytic Stripper-module (CS) vs. Evaporation-Tube module (ET) particle penetration

To determine size dependent particle penetration dependencies of a standard SPCS ET module compared to the CS module of the PEMs4Nano LabSystem, the AVACS setup was used in the configuration shown in Figure 4-3.



Figure 4-3: AVACS setup measurements of particle penetration of PNCS components.

For being able to easily cancel out line-losses in the respective lines, the line to the reference CPC1 was exactly double the respective line leading to the DUT_x and the line from DUT_x to CPC_i .

Using this setup, 6 scans with 25 size steps each each were performed with DUT_x temperatures at room-temperature (25°C) as well as heated to temperatures of 250°C, 300°C, 350°C and 400°C. The resulting penetration curves are shown in Figure 4-4. All data shown is corrected for CPC-flow, -coincidence as well as CPC intercalibration of Figure 4-2.





Figure 4-4: ET (dashed-lines) and CS (solid-lines) particle penetration curves at different set temperatures.

Regarding these results at room temperature and large particles, the cold ET shows a penetration of 99,8%. These expected small extra losses imposed only by the cold stainless-steel tube is proving the in principle working methodology of these penetration tests after appliance of the CPC intercalibration factors. The cold CS shows a smaller penetration of 97,5% as expected due to the extra volume and catalytic substrate in the aerosol stream imposing losses. However, going to small particles (14 nm), the CS already drops to a penetration of 61,5% compared to the ETs 83,6%. These doubled losses at 14 nm compared to the traditional ET are already showing some need for further optimization of the used CS for future generations.

Now regarding the penetration curves of the heated DUTs, overall penetration drops by approx. 30% due to higher diffusional and thermophoretic losses at higher temperatures. However, a retrospect comparison of these loss factors with effectively smaller overall VPR PCRF factors presented in subsequent section 5.1, the absolute losses determined with the methodology here are overestimated. This is probably due to additional thermophoretic losses of the heated aerosol leaving the DUTs while being transferred to the CPCs in uncooled lines – an effect which doesn't appear in PMP VPR setups due to immediate cooling by dilution in PND2. Consequently, only relative differences of the ET and CS-penetration factors at same temperatures can be regarded here for discussion - with room for further optimization of this methodology in future investigations.

With CS penetration for larger particles being slightly higher than the corresponding ET-factors (caused by a shorter heated section in CS imposing losses), particle losses at small particles show the same trend of noteworthy higher relative losses which exhibits a relative extent similar to the room temperature measurement.

Altogether, the results of Figure 4-4 nevertheless exhibit a very good comparability with the PEMs4Nano WP1 deliverable D1.01 expectations shown in D1.01-Figure 3.2.

Due to these results, further investigations and optimizations with the goal to decrease small particle losses whilst maintaining sufficient removal of volatile components will be conducted in the PEMs4Nano project by the Boies group at University of Cambridge. These optimized components will be directly implemented in the succeeding PEMs4Nano PEMS Sub-23 nm system – and a later upgrade of the current PEMs4Nano LabSystem's CS will be considered too, regarding the achievable improvements.



4.3 CPC

The calibration of the 10 nm CPC for the PEMs4Nano LabSystem already was documented in the PEMs4Nano deliverable report D2.02. As this CPC with its calibration now became an integral part of the PEMs4Nano LabSystem, final calibration results should be repeated here briefly with the calibration Table 4-2 (with the k-factor programmed into the PEMs4Nano LabSystem) and the size-dependent CPC cut-off characteristic in Figure 4-5.

 Table 4-2: TSI PEMs4Nano 10 nm CPC calibration: Data for the determination of the size dependent detection efficiencies of the 10 nm lab CPC for PAO calibration particles.

	Ini	tial detection effi	ciency measurem	ent
Particle diameter (nm)	10 nm	15 nm	23 nm	55 nm
Reference concentration (cm ⁻³)	5511	5484	5151	5972
UUT concentration [cm ⁻³]	3883	4941	4862	5757
Detection efficiency (%) w/o k-factor	70,5	90,1	94,4	96,4
Rel. uncertainty (%, k=2)	3,95	4,14	3,52	3,58
k-factor		1,0	327	
Detection efficiency (%) with k-factor	72,8	93,0	97,5	99,6



Figure 4-5: TSI PEMs4Nano 10 nm CPC calibration: Size dependent detection efficiencies of the 10 nm lab CPC for PAO calibration particles with and without k-factor.



5 PEMs4Nano LabSystem – Calibration results

According to HORIBA PNCS calibration methodology described section 3.1, the HORIBA PEMs4Nano LabSystem has undergone PCRF calibration measurements pre-modification (standard HORIBA SPCS-2100) and after the modifications performed resulting in the PEMs4Nano LabSystem:

- 1. Initial SPCS calibration of original SPCS at the manufacturing site at HORIBA Japan (HOR, pre-modification, standard calibration as performed on any new SPCS system).
 - Original system equipped with standard ET (and standard 23 nm CPC100)
 - Calibration (LCU) particle sizes: 100 nm, 50 nm, 30 nm (PMP-standard)
- 2. PEMs4Nano calibration after PEMs4Nano modifications at HORIBA Germany (HE, post-modification).
 - Modified system equipped with CS (and CPC100 calibrated to 10 nm)
 - Calibration (LCU) particle sizes: 100 nm, 50 nm, 30 nm plus 23 nm & 15 nm

Unfortunately, pre-modification measurements couldn't be repeated with the extended range of particle sizes at HORIBA Germany due to time limitations in instrument availability before modification.

5.1 PEMs4Nano LabSystem – VPR PCRF calibration

Absolute values

Figure 5-1 shows the PCRF results of the original system in grey bars (SPCS (ET)) as well as of the modified PEMs4Nano LabSystem in blue bars (SPCS (CS)). Each block of data represents one of the five available & calibrated dilution settings, and each block is containing the different PCRF calibration particle sizes:



Figure 5-1: PEMs4Nano LabSystem – PCRF calibration – Absolute values over all dilution-settings (Dil) and particle size (D_P).

As anticipated, particle losses / PCRF-factors increase after exchanging the original ET with the CS. Adding 23 nm and 15 nm size values did work well and did lead to valid measurements results using the given HORIBA PCRF calibration setup, LCU model aerosol and calibration methodology. Thus, this extended calibration work can be fitted to the existing calibration facility. Plausibility of single PCRF measurements is fully given with all the absolute values in the expected ranges, and losses monotonously increasing going to smaller particles.



Dilution-normalized values

To gain a better relative insight to relative particle losses, PCRF-values now will be normalized to the respective dilution-setting (Dil) in the following Figure 5-2:



Figure 5-2: PEMs4Nano LabSystem – PCRF calibration – Dilution-normalized values over all dilution-settings (Dil) and particle size (D_P) (normalized to dilution factor).

Regarding the lower dilution settings of 150 and 200 in Figure 5-2, PCRF values of larger particles sizes are not strongly deviating with the CS installed compared to the original ET values. This agrees with previous basic measurements of the components itself discussed in section 4.2. However, increased CS particle losses can already be recognized at 30 nm particle sizes. Differences between CS and ET measurements become slightly larger going to higher dilution-settings, which can be explained by the decreased Flow-Orifice (FO-1) flows in SPCS and thus slightly larger residence times during high dilution.

Raw calibration data

Table 5-1 reports the full calibration data set in the format of the HORIBA SPCS maintenance & calibration report, with small particle sizes of 23 nm and 15 nm added. Regarding absolute values of classified LCU particle generator PN- concentration, absolute concentrations were sufficient, ranging from 8377 to 59309 #/cm³ (Step 1 & Step 3) - which also led to good statistics of the measurement of the small outlet concentrations (Step 2) after dilution & losses. Though, calibration points of the very high dilution setting of 3000 regarding both extreme small and large particle sizes result in very small outlet concentrations being on the lower threshold for measurement with the current UFCPC setup. However, it is very unlikely that modern engine generations in question to be measured with any sub-23 nm PN methodology will require both the highest dilution settings due to their low engine-out and/or post-EAT PN emissions even during cold-start, thus leaving these dilution settings being optional for some R&D work, but non-necessary for certification purposes.

The stability of LCU particle generation between Step 1 and Step 3 ("LCU stability error") was very good with values smaller than 3-4 % despite the long time with all dilution settings being calibrated in the intermediate Step 2. Consequently, influence of LCU stability will be well below < 1,5-2 % after averaging of the small monotonous drifts occurring. Any influences could be further reduced with additional reference measurements (additional reference-step or additional reference CPC), but prove not to be necessary using the current LCU aerosol.



Table 5-1: PEMs4Nano LabSystem – PCRF calibration – Raw calibration results.

			Step 1	Step 2	Step 3			
PND 1	PND 2	Particle Size	Inlet Conc. #1 (#/cm ³)	Outlet Conc. (#/cm ³)	Re-Inlet Conc. #2 (#/cm ³)	LCU Stability Error	PCRF fr(d)	ratio*
10	15	15	8377,3	34,2	8716,4	4,05%	250,27	1,57
10	15	23	42004,0	195,8	42509,8	1,20%	215,82	1,36
10	15	30	59309,0	307,6	59083,2	-0,38%	192,45	1,21
10	15	50	54690,5	310,4	53113,7	-2,88%	173,65	1,09
10	15	100	12420,1	77,0	12092,4	-2,64%	159,17	
20	15	15	8377,3	18,9	8716,4	4,05%	453,41	1,36
20	15	23	42004,0	96,4	42509,8	1,20%	438,35	1,31
20	15	30	59309,0	151,2	59083,2	-0,38%	391,51	1,17
20	15	50	54690,5	152,3	53113,7	-2,88%	353,92	1,06
20	15	100	12420,1	36,7	12092,4	-2,64%	333,96	
50	15	15	8377,3	6,3	8716,4	4,05%	1362,05	1,58
50	15	23	42004,0	36,9	42509,8	1,20%	1145,17	1,33
50	15	30	59309,0	58,0	59083,2	-0,38%	1020,62	1,18
50	15	50	54690,5	56,6	53113,7	-2,88%	952,33	1,10
50	15	100	12420,1	14,2	12092,4	-2,64%	863,12	
100	15	15	8377,3	3,4	8716,4	4,05%	2499,08	1,54
100	15	23	42004,0	18,2	42509,8	1,20%	2321,81	1,43
100	15	30	59309,0	28,3	59083,2	-0,38%	2091,73	1,29
100	15	50	54690,5	29,7	53113,7	-2,88%	1814,89	1,12
100	15	100	12420,1	7,6	12092,4	-2,64%	1617,99	
200	15	15	8377,3	1,8	8716,4	4,05%	4883,91	1,28
200	15	23	42004,0	9,1	42509,8	1,20%	4643,62	1,22
200	15	30	59309,0	14,2	59083,2	-0,38%	4168,74	1,09
200	15	50	54690,5	14,4	53113,7	-2,88%	3743,20	0,98
200	15	100	12420,1	3,2	12092,4	-2,64%	3809,84	

Following the above considerations regarding small particle concentrations, an additional 10 nm PCRF measurement has been tested with the current setup, but data had to be discarded due to non-sufficient particle concentrations. Though using a further diluted LCU NaCl solution led to smaller particle size distributions, concentrations in the current setup still were very small. Moreover, such an approach would lead to a high increase in calibration throughput time and complexity due to the necessity of exchanging the solution and stabilizing time in current HORIBA methodology as well as non-conformity with calibration methodology of all other current HORIBA laboratory systems. Thus, this approach was not followed in the current campaign intended to maintain best consistency with current methodology.

However, investigations of using alternative calibration aerosols (particularly cast aerosol) might be an option for future optimizations, also leading to the usage of the same soot-like cast-aerosol as used in the 10 nm CPC calibration (compare section 4.3 and D2.02) as well as calibration of the HORIBA PEMS-PN systems, but were out of the scope of the current report also intended to lead to a fast reliability of the PEMs4Nano LabSystem for subsequent tests at the single- and multi-cylinder engine test beds. During future calibration work for the PEMs4Nano PEMS-system, this will be investigated more for both the Lab- and the PEMS-system.



PCRF(100nm)-normalized values

PMP also specifies the allowable ratio of the small particle sizes PCRF-values compared to the PCRF(100 nm)-values (compare section 2.4.1):

$$0.95 \leq PCRF(50nm, Dil_{SPCS,i}) / PCRF(100nm, Dil_{SPCS,i}) \leq 1.20.$$
 (Eq. 5-1)

$$0.95 \leq PCRF(30nm, Dil_{SPCS,i}) / PCRF(100nm, Dil_{SPCS,i}) \leq 1.30.$$
 (Eq. 5-2)

Figure 5-3 now normalizes all measured PCRF values to $PCRF(100nm, Dil_{SPCS,i})$. The areas of ratios of (Eq. 5-1) and (Eq. 5-2) are marked by respective green boxes. Moreover, following possible ratios for 23 nm and 15 nm are indicated by light green boxes, as a suggestion for a future extension of the above ratios to smaller particle setpoints:

$$0.95 \le PCRF(23nm, Dil_{SPCS,i}) / PCRF(100nm, Dil_{SPCS,i}) \le 1.40.$$
 (Eq. 5-3)

$$0,95 \le PCRF(15nm, Dil_{SPCS,i}) / PCRF(100nm, Dil_{SPCS,i}) \le 1,60.$$
(Eq. 5-4)



Figure 5-3: PEMs4Nano LabSystem – PCRF calibration – PCRF100-normalized values over all dilution-settings (Dil) and particle size (D_P) (normalized to PCRF(100nm, Dil)).

The pre-modified SPCS using the ET is easily achieving both the original 50 nm and 30 nm PCRF-ratios. Furthermore – and especially noteworthy – even the modified PEMs4Nano LabSystem ratios with the CS installed still are within original PMP recommendations, despite the higher particle losses induced by the CS. Neglecting the only measurement point approaching the 130 % limit (Dil=1500, D_P =30nm, ratio=1,29) possibly being a small positive outlier, the rest of the LabSystem's ratios are near 110 % for 50 nm and 120 % for 30 nm.

→ As a result, the modified PEMs4Nano LabSystem still is fully compliant to the PMPrecommendations and thus the ECE-R83 and ECE-R49 regulation limits for PCRF calibration of particle number counting systems.



Averaged $\overline{PCRF_{xx-100}}$ values – Final $\overline{PCRF_{xx-100}}$ calibration

According to the different possible definitions for the calculation of the \overline{PCRF} -average, all definitions given in Equations (Eq. 3-7), (Eq. 3-8), (Eq. 3-9) were used in \overline{PCRF}_{xx-100} calculations, with results drawn in Figure 5-4 and final values given in Table 5-2. \overline{PCRF}_{30-100} is the PMP standard \overline{PCRF} , averaging 100 nm, 50 nm and 30 nm measurements. \overline{PCRF}_{23-100} additionally includes 23 nm and \overline{PCRF}_{15-100} additionally includes 23 nm and 15 nm, thus leading to higher factors due to increased particle losses going to smaller particle sizes. HE-results of these different definitions are drawn in blue nuances for the PEMs4Nano LabSystem, whereas the HOR-results of the original non-modified, ET-equipped SPCS are drawn in grey for comparison.



Figure 5-4: PEMs4Nano LabSystem – PCRF calibration – Averaged PCRF values over all dilution-settings (Dil) for different definitions of $\overline{PCRF_{xx-100}}$.

Left graph: Absolute values; Right Graph: Values normalized with respective dilution-ratio.

Grey bars: Original, ET-equipped, non-modified SPCS-2100 system; Blue bars: CS-equipped, modified PEMs4Nano LabSystem.

Analyzing the final values given in Table 5-2, following conclusions can be drawn:

- Regarding PCRF₃₀₋₁₀₀, the impact of the modification from SPCS-ET to SPCS-CS is an increase of PCRF-factor by only 1,0 12,5 % (again, neglecting the highest dilution). Besides showing a fully acceptable increase of the absolute value, also a very good consensus of the PCRF calibration performed by HORIBA Japan and HORIBA Germany facilities can be concluded (also see following DSU-PCRF-calibration): Here, differences of ET- versus CS-penetration come together with inevitable small differences in calibration laboratories (however, differences being small due to HORIBA PCRF calibration methodology only using relative measurements).
- Regarding $\overline{PCRF_{23-100}}$ compared to, $\overline{PCRF_{30-100}}$, the extension of the PCRF-definition by a 23 nm setpoint only increases the PCRF value by approximately 5 %.
- Regarding $\overline{PCRF_{15-100}}$ compared to, $\overline{PCRF_{30-100}}$, the extension of the PCRF-definition by both 23 nm and 15 nm setpoints increases the PCRF value by approximately 10 13 %. Though small particles PCRF values are noteworthily higher, their addition to the PCRF definition only leads to a fractional influence in the overall average.



Table 5-2: PEMs4Nano LabSystem – PCRF calibration –Averaged $\overline{PCRF_{xx-100}}$ calibration values and ratios.

PCRF measurement	Dilution (Dil)	PND1	PND2	ď	PCRF(D _P)	Ratio	PCRF ₃₀₋₁₀₀	PCRF ₃₀₋₁₀₀	PCRF ₂₃₋₁₀₀	PCRF ₁₅₋₁₀₀	PCRF(D _P)	PCRF ₃₀₋₁₀₀ /	PCRF ₂₃₋₁₀₀ /	PCRF ₁₅₋₁₀₀
point					(SPCS-CS)	PCRF(D _P) / PCRF(100nm)	(SPCS-ET)	(SPCS-CS)	(SPCS-CS)	(SPCS-CS)	Dil	Dil	Dil	Dil
Dil=150, Dp=15	150	10	15	15	250,27	1,57					1,67			
Dil=150, Dp=23	150	10	15	23	215,82	1,36					1,44			
Dil=150, Dp=30	150	10	15	30	192,45	1,21					1,28			
Dil=150, Dp=50	150	10	15	50	173,65	1,09	173,36	175,09	185,27	198,27	1,16	1,17	1,24	1,32
Dil=150, Dp=100	150	10	15	100	159,17	1,00		(+ 0,99% to SPCS-ET)	(+ 5,81% to PCRF30-100)	(+ 13,24% to PCRF30-100)	1,06			
Dil=300, Dp=15	300	20	15	15	462,41	1,38					1,54			
Dil=300, Dp=23	300	20	15	23	438,35	1,31					1,46			
Dil=300, Dp=30	300	20	15	30	391,51	1,17					1,31			
Dil=300, Dp=50	300	20	15	50	353,92	1,06	343,96	359,80	379,43	396,03	1,18	1,20	1,26	1,32
Dil=300, Dp=100	300	20	15	100	333,96	1,00		(+ 4,6% to	(+ 5,45% to	(+ 10,07% to	1,11			
Dil=750. Do=15	750	50	15	15	1362.05	1.58		Jrug-Lu			1.82			
Dil=750, Dp=23	750	50	15	23	1145,17	1,33					1,53			
Dil=750, Dp=30	750	50	15	30	1020,62	1,18					1,36			
Dil=750, Dp=50	750	50	15	50	952,33	1,10	840,39	945,36	995,31	1068,66	1,27	1,26	1,33	1,42
Dil=750, Dp=100	750	50	15	100	863,12	1,00		(+ 12,48% to	(+ 5,28% to	(+ 13,04% to	1,15			
								SPCS-ET)	PCRF30-100)	PCRF30-100)				
Dil=1500, Dp=15	1500	100	15	15	2499,08	1,54					1,67			
Dil=1500, Dp=23	1500	100	15	23	2321,81	1,43					1,55			
Dil=1500, Dp=30	1500	100	15	30	2091,73	1,29					1,39			
Dil=1500, Dp=50	1500	100	15	50	1814,89	1,12	1725,36	1841,54	1961,60	2069,10	1,21	1,23	1,31	1,38
Dil=1500, Dp=100	1500	100	15	100	1617,99	1,00		(+ 6,73% to SPCS-FT)	(+ 6,51% to PCRF30-100)	(+ 12,35% to PCRF30-100)	1,08			
Dil=3000, Dp=15	3000	200	15	15	4883,91	1,28		l		(1,63			
Dil=3000, Dp=23	3000	200	15	23	4643,62	1,22					1,55			
Dil=3000, Dp=30	3000	200	15	30	4168,74	1,09					1,39			
Dil=3000, Dp=50	3000	200	15	50	3743,20	0,98	3293,84	3907,26	4091,35	4249,86	1,25	1,30	1,36	1,42
Dil=3000, Dp=100	3000	200	15	100	3809,84	1,00		(+ 18,62% to SPCS-ET)	(+ 4,71% to PCRF30-100)	(+ 8,76% to PCRF30-100)	1,27			



5.2 PEMs4Nano LabSystem – DSU PCRF calibration

According to the HORIBA DSU calibration methodology described in section 3.3, the DSU unit of the PEMs4Nano LabSystem also has been calibrated at both the HORIBA Japan (HOR) and the HORIBA Germany (HE) facilities. Whereas the Sub-23 nm modifications to the PEMs4Nano SPCS system itself have no influence on the DSU-unit itself, the system was re-equipped in HE by a new 4 m heated PTT designed for the European market (same length but different make compared to the heated PTT used during HOR calibration). Moreover, the additional PCRF setpoints of 23 nm and 15 nm have been added during the second calibration on Germany.

Concurrent as performed in the preceding VPR PCRF calibration, the different possible definitions for the calculation of the \overline{PCRF} -average were similarly used in $\overline{PCRF}_{DSU,xx-100}$ calculations ($\overline{PCRF}_{DSU,30-100}$, $\overline{PCRF}_{DSU,23-100}$, $\overline{PCRF}_{DSU,15-100}$) with results drawn in the right Figure 5-4.



Figure 5-5: PEMs4Nano LabSystem – DSU PCRF calibration Left Graph: Absolute DSU-PCRF values over particle size (DP). Right Graph: Averaged DSU PCRF values over for different definitions of $\overline{PCRF_{DSU,xx-100}}$.

Also analyzing the final values given in Table 5-3, following conclusions can be drawn:

- Results of $\overline{PCRF_{DSU,30-100}}$ independently determined at the HOR (grey) and HE (dark blue) facilities only deviate by a very small value of 2,3 %. Thus, a very good worldwide reproducibility using the HORIBA PRCF methodology can be concluded.
- Going to $\overline{PCRF_{DSU,23-100}}$ only leads to a relative increase of 6,7 % which is similar to the increases observed during VPR calibration. However, this is rather coincidence as components causing particle losses are completely different now (DSU plus PTT compared to VPR equipped with CS).
- Going to *PCRF_{DSU,15-100}* leads to a relative increase of 13,8 % also similar to the increases observed during VPR calibration.



Table 5-3: PEMs4Nano LabSystem – DSU PCRF calibration – Averaged $\overline{PCRF_{DSU,xx-100}}$ calibration values and ratios.

PCRF measurement point	Dilution (Dil)	PND1	PND2	D _P	PCRF(D _P) (SPCS-CS)	Ratio PCRF(D _P) / PCRF(100nm)	PCRF ₃₀₋₁₀₀ (SPCS-ET)	PCRF ₃₀₋₁₀₀ (SPCS-CS)	PCRF ₂₃₋₁₀₀ (SPCS-CS)	PCRF ₁₅₋₁₀₀ (SPCS-CS)	PFRF(D _P) / Dil	PCRF ₃₀₋₁₀₀ / Dil	PCRF ₂₃₋₁₀₀ / Dil	PCRF ₁₅₋₁₀₀ / Dil
Dil=10, Dp=15	10	10	1	15	17,30369755	1,437847924					1,73			
Dil=10, Dp=23	10	10	1	23	15,41378832	1,280806225					1,54			
Dil=10, Dp=30	10	10	1	30	12,59304888	1,046417342					1,26			
Dil=10, Dp=50	10	10	1	50	11,85709329	0,985263233	11,89	12,16	12,97	13,84	1,19	1,22	1,30	1,38
								(+ 2,28% to	(+ 6,68% to	(+ 13,8% to	1,20			
Dil=10, Dp=100	10	10	1	100	12,03	1,00		SPCS-ET)	PCRF30-100)	PCRF30-100)				

5.3 PEMs4Nano LabSystem – Summary of programmed calibration data

All final $\overline{PCRF(D\iota l)}$ that can be programmed into the PEMs4Nano LabSystem are summarized in Table 5-4 for all dilutions settings being available.

Table 5-4: PEMs4Nano LabSystem – Summary of VPR and DSU calibration – Final PCRF factors to be programmed to SPCS.

Dilution (Dil)	PND1	PND2	PCRF ₃₀₋₁₀₀	PCRF ₂₃₋₁₀₀	PCRF ₁₅₋₁₀₀
150	10	15	175,09	185,27	198,27
300	20	15	359,80	379,43	396,03
750	50	15	945,36	995,31	1068,66
1500	100	15	1841,54	1961,60	2069,10
3000	200	15	3907,26	4091,35	4249,86
DSU	x 1	.0	12,16	12,97	13,84

Due to the lack of any agreement on exact $\overline{PCRF_{xx-100}}$ – definition during Sub-23 nm measurements in the current PMP- or other working groups, it was chosen to initially program the PEMs4Nano LabSystem with the conventional $\overline{PCRF_{30-100}}$ values of standard PMP. This has the advantage that comparing measurement results of the PEMs4Nano LabSystem with these of a conventional 23 nm SPCS or other PMP instrument will only show intrinsic differences due to actual different instrument particle counting efficiency due to increased detector size range and CS-losses of the PEMs4Nano LabSystem – and not additional effects of any extended $\overline{PCRF_{xx-100}}$ definition.

However, an easy re-calculation to any other $\overline{PCRF_{xx-100}}$ definition can be done also during post-processing, as measurement data with an applied $\overline{PCRF_{30-100}}$ can be inversed since the factor is only a constant (non-size- and concentration-dependent-) factor applied in the last step of PNCS inlet calculation.

The official HORIBA SPCS maintenance & calibration report containing all results of this report will be provided to the subsequent PEMs4Nano-users together with the PEMs4Nano LabSystem. However, it needs to be considered that this system – though exhibiting PMP-valid PCRF results – nonetheless is not accredited for any certification PN-measurement due to the PEMs4Nano 10 nm CPC deployed.



6 Conclusions

In this report, it was successfully demonstrated that the modification of the well-proven HORIBA MEXA-2100 concept for enabling the PNCS for sub-23 nm measurements - as well as an extended VPR PCRF calibration using smaller particles sizes under the HORIBA PCRF calibration methodology - is feasible.

This lead to the PEMs4nano LabSystem prototype equipped with a hot catalytic stripper and the 10 nm CPC10 of PEMs4Nano deliverable D2.02.

Considering specifications of PMP-based regulations for PN-counting (e.g. ECE-R84, ECE-R49), the modified PEMs4Nano LabSystem still is fully compliant to the PMP-recommendations for the VPR despite extra losses induced by the installed CS compared to the original ET.

New calibration factors according to three different definitions for a \overline{PCRF} -average for the VPR ($\overline{PCRF_{30-100}}$, $\overline{PCRF_{23-100}}$, $\overline{PCRF_{15-100}}$) as well as for the DSU ($\overline{PCRF_{DSU,30-100}}$, $\overline{PCRF_{DSU,23-100}}$, $\overline{PCRF_{DSU,15-100}}$) have been established and will be supplied with the prototype. With the standard PMP definition being programmed into the system, an easy re-calculation to the extended definitions of the average can be performed for discussions of any future regulation.

In the next steps, the PEMs4Nano LabSystem will be transferred to the engine emissions facilities of first Bosch for tests at their Single-Cylinder as well as their Multi-Cylinder-engines and subsequently to IDIADA for vehicle tests and the engine dyno together with the forthcoming PEMs4Nano PEMS-system prototype.



7 Recommendations

After the final IDIADA tests and possibly in between campaigns during the transfer time from Bosch to IDIADA, it can be considered to perform a validation of the PEMs4Nano LabSystem PCRF calibration data which was now first established in this report – to ensure as well as to investigate and report the stability of the added small particle PCRF factors.

It will be recommended, that engine tests will be performed with the now given possibility of a parallel measurement with the PEMs4Nano 10 nm CPC (PN₁₀) as well as the original 23 nm PMP CPC (PN₂₃). The additional 23 nm can be temporarily supplied with the PEMs4Nano LabSystem. This will give additional valuable insight, for example:

- Determination of overall PN₁₀/PN₂₃ emission factors and range of PN increase by change of D₅₀, regarding the differing engines, engine operation points and engine-preconditions.
- Estimation of changes in and effects on particle size distribution by analyzing changes in PN₁₀(t)/PN₂₃(t) ratios (larger ratio is corresponding to smaller size distributions).
- In case particles are only detected on the PN₁₀ counter, thus sole nucleation-mode particles being detected: Creation of a methodology to further understand and discriminate the nature of such a mode which might be a volatile-only artifact (implying non-sufficient CS efficiency) on the one side or a semi-volatile nucleation mode or even a 'solid particle nucleation mode' on the other side. In the latter case, particle characteristics, morphology and composition should be deliberately analyzed by the extensive set of additional analytic methods (SEM, TEM, AFM-Raman/TERS, L2MS, SIMS) available in the PEMs4Nano project to understand origins and causes of such "solid nucleation mode particles" (e.g. engine-oil consumption, ...).

Considering the PEMs4Nano LabSystem as well as PEMs4Nano PEMS-System development:

- Overall CS particle penetration has potential to be further increased in the future (Boies group @ UCAM).
- Further investigations for increase of DSU, PND1 and PND2 small particle penetration may be performed under the premise of maintaining consistency with current SPCS basic setup and calibration methodology.

Considering any final definitions of extended exact $\overline{PCRF_{xx-100}}$ -factors also including smaller particle sizes, it should be suggested that PCRF sizes to be included should deliberately be weighted considering statistics of real emitted size distributions of currently prevailing modern engine concepts, also regarding the respective influence on the PN value by weighting with the overall PNCS size dependent efficiency. For the acceptance for both the industry stakeholders on the one side, and legislative stakeholders and public notion on the other side, it should be investigated whether such an approach can lead to a possibility to maintain reasonable consistency with traditional PMP PN measurements as well as avoiding significant portions of solid particles not being taken account for in future certification measurements.



8 Deviations from Annex 1

There are no deviations from Annex 1 to report.



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P	roject	partners:		
	#	Туре	Partner	Partner Full Name
	1	IND	HORIBA	HORIBA Europe GmbH
	2	IND	Bosch	Robert Bosch GmbH
	3	IND/SME	CMCL	Computational Modelling Cambridge Limited
	4	IND	TSI	TSI GmbH
	5	HE	UCAM	The Chancellor, Masters and scholars of the University of Cambridge
	6	HE	ULL	Université des Sciences et Technologies De Lille – Lille I
	7	IND	IDIADA	Idiada Automotive Technologie SA
	8	IND	HORJY	HORIBA Jobin Yvon S.A.S.
	9	IND/SME	UNR	Uniresearch BV



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Appendix A – Quality Assurance

The following questions should be answered by all reviewers (WP Leader, peer reviewer 1, peer reviewer 2 and the technical coordinator) as part of the Quality Assurance Procedure. Questions answered with NO should be motivated. The author will then make an updated version of the Deliverable. When all reviewers have answered all questions with YES, only then the Deliverable can be submitted to the EC.

NOTE: For public documents this Quality Assurance part will be removed before publication.

Questi	on	WP Leader	Peer reviewer 1	Peer reviewer 2	Technical
					Coordinator
		Thomas Maier	Hans-Georg Horn	Cristian Focsa	Marcus Rieker
		(Horiba)	(TSI)	(ULL)	(Horiba)
1.	Do you accept this deliverable as	Yes	Yes	Yes	Yes
2.	Is the deliverable completely ready? If not, please indicate and motivate required	Yes	Yes	Yes	Yes
3.	Does this deliverable correspond to the DoW?	Yes	Yes	Yes	Yes
4.	Is the Deliverable in line with the PEMs4Nano objectives?	Yes	Yes	Yes	Yes
a.	WP Objectives?	Yes	Yes	Yes	Yes
b.	Task Obiectives?	Yes	Yes	Yes	Yes
5.	Is the technical quality sufficient?	Yes	Yes	Yes	Yes



Appendix B – Abbreviations / Nomenclature

Table B-1 List of Abbreviations / Nomenclature.

Symbol / Shortname	
AVACS	Automated Validation and Calibration System (for HORIBA SPCS).
С	Particle number concentration (in #/cm ³).
$c_X(D_P)$	Size-dependent particle concentration (in #/cm ³ /nm).
СЕО	Critical Flow Orifice.
СРС	Condensation Particle Counter.
CPC100	CPC used in SPCS2x000 systems, OEM version based on TSI full-flow EECPC series, originally calibrated to a D_{50} of 23 nm.
СРС3776	Ultrafine CPC with a D_{50} of 2,5 nm (used for PCRF calibration).
cut-off, cut-off-curve	Used either as single particle size value of CPC's 50% counting efficiency (see D ₅₀) or in terms of a cut-off-curve indicating an instruments/CPC's size dependent counting efficiency characteristic (also see $\eta_X(D_P)$).
CVS	Constant Volume Sampling (dilution system / dilution tunnel using full-flow exhaust dilution).
D ₅₀	Particle size of instrument/CPC's 50% counting efficiency (also see cut-off).
Dp	Particle diameter in nm (also see GMD).
DI-(engine)	Direct Injection (engine).
DMA	Differential Mobility Analyzer: strictly only the electrostatic classifying column of a particle size classifier system (e.g. TSI 3081), sometimes synonymously used for the whole classifying system (e.g. TSI 3080).
DPF	Diesel Particulate Filter (EAT device).
DSU	(HORIBA) Direct Sampling Unit (1:10 pre-dilution unit for raw-exhaust measurements).
Dil / DF	Dilution Setting, Dilution Factor (Dilution Ratio).
DUT	Device Under Test.
EAT	Exhaust After Treatment (e.g. TWC, DPF, SCR).
(UN)ECE	(United Nations) Economic Commission for Europe.
ECE-R	Regulation of the (UN)ECE.
EECPC	Engine Exhaust CPC (e.g. TSI CPC3790/3791, CPC100).
ET	Evaporation Tube.
FCAE	Faraday Cup Aerosol Electrometer.
FO	Flow Orifice, flow measurement using absolute- and differential pressure over an orifice as well as gas temperature.
GMD	Geometric Mean Diameter (of a particle size distribution).
GST	Geometric Standard Deviation (of a particle size distribution).
НЕРА	High-Efficiency Particulate Air (Filter).
$\eta_X(D_P)$	Size-dependent particle penetration efficiency or size-dependent counting efficiency characteristic of component/instrument X.
HD	Heavy-Duty (-vehicle / -engine).
HE	HORIBA Europe.
HOR	HORIBA Japan.



ICE	Internal Combustion Engine.
k	k-factor (CPC calibration factor from inverse linear regression slope).
LCU	(HORIBA) Linearity Check Unit (NaCl atomizer & particle generator).
LD	Light-Duty (-vehicle / -engine).
MEXA	(HORIBA) Multicomponent motor Exhaust Analyzer.
MFC	(thermal) Mass Flow Controller.
N	(Particle) Number.
NaCl	Sodium Chloride.
Nlpm	"Norm"-liter per minute normalized to 273,3 K (0°C) @ 101,3 kPa conditions
PEMs4Nano	PEMs4Nano.
PEMs4Nano LabSystem	PEMS4Nano laboratory PN counting system modified with CS and 10 nm CPC (based on HORIBA MEXA SPCS-2100).
PEMs4Nano PEMS-System	PEMS4Nano (mobile) PEMS PN counting system with modified CS and compact 10 nm CPC (based on HORIBA OBS-PN).
ΡΑΟ	Poly-Alpha-Olefin (calibration aerosol material, commonly called "EmeryOil").
PCRF	Particle Count Reduction Factor.
PEMS	Portable Emissions Measurement System (for RDE tests).
PFDS	Partial Flow Dilution System (dilution system using partial & proportional exhaust dilution).
РМР	Particle Measurement Programme.
PN	Particle Number.
PNCS	Particle Number Counting System (PMP system).
PND (PND0, PND1, PND2)	Particle Number Diluter (pre-diluter, VPR 1 st PND, VPR 2 nd PND).
PSP	Particle Sampling Probe (PSP).
PTS	Particle Transfer System (includes PSP and PTT).
РТТ	Particle Transfer Tube (tubing from either CVS, PFDS or DSU to PNCS input.
R ²	Coefficient of determination (here: for linear regression).
R&D	Research & Development (commonly used also for R&D PN measurements not under certification conditions).
REF	Reference (instrument/sensor/CPC).
SCR	Selective Catalytic Reduction (-EAT device).
Slpm	"Standard"-liter per minute normalized to 294.3 K (21,1°C) @ 101,3 kPa conditions ("TSI standard conditions").
SMPS	Scanning Mobility Particle Sizer.
SPCS	Solid Particle Counting System (HORIBA PNCS).
SPCS-ET	Standard SPCS equipped with Evaporation Tube (standard SPCS system).
SPCS-CS	Modified SPCS equipped with Catalytic Stripper (see PEMs4Nano LabSystem).
Sub-23 nm	Prefix referring to any PN measurement with an instrument efficiency adjusted to be more sensitive to particles below 23 nm than conventional PMP-setups. Most commonly, a D_{50} of 10 nm is discussed for the CPC.
TD	Thermo-Denuder.
тwс	Three Way Catalyst (EAT device).



UFCPC	Ultrafine CPC.
UNECE	(United Nations) Economic Commission for Europe.
VPR	Volatile Particle Remover.