Understanding, Measuring and Regulating Sub-23 nm Particle Emissions from Direct Injection Engines Including Real Driving Conditions

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Introduction

The present document describes the deliverable D2.5 of Project SUREAL-23. This deliverable concerns the Sizing Condensation Particle Counter suitable for measurements of sub-23 particles emitted from engine exhaust. The document summarizes the development and testing of such instrument. 2 Prototype instruments will be built, and calibrated. These prototypes will be available to be used in further parts of the SUREAL project by other partners.

Abbreviations list

EC	European Commission
EU	European Union
GA	General Agreement
R&D	Research and Development
RTD	Research and Technological Development
D	Deliverable
DAQ	Data Acquisition
CA	Consortium Agreement
GA	Grant Agreement
INEA	Innovation Networks Executive Agency
M	Month
MS	Milestone
PC	Project Coordinator
WP	Work Package
DMA	Differential Mobility Analyzer
HM	Half Mini
THABr	Tetraheptylammonium bromide
S-CPC	Sizing Condensation Particle Counter

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Short Project Overview

A large proportion of the total number of particles emitted from direct injection engines is below 23 nm and although the EU aims to regulate those emissions and impose limits for new light duty vehicles, this is not yet possible due to the absence of accurate quantification methods, especially under real driving conditions. The main reason for this is the absence of adequate knowledge regarding the nature of sub-23 nm particles from different engine/fuel combinations under different operating conditions. SUREAL-23 aims to overcome such barriers by introducing novel measurement technology for concentration/size/composition measurements. The recently established supercontinuum laser technology will be coupled to photoacoustic analysis and will also be employed for photoelectric ionization aerosol charging to achieve real-time, composition size-specific analysis of the particles. In parallel, state of the art aerosol measurement techniques will be advanced for better compatibility with sub-23 nm exhaust particles as well as on-board use. The developed instrumentation will assess sub-23 nm particle emissions from both Diesel and GDI vehicles accounting for effects of the fuel, lubricants, after treatment and driving conditions for existing and near-future vehicle configurations. The most suitable concepts will be developed for PN-PEMS applications and evaluated accordingly. The project will provide measurement technologies that will complement and extend established particle measurement protocols, sustaining the extensive investments that have already been made by industry and regulation authorities. The project will deliver systematic characterization of sub 23-nm particles to facilitate future particle emission regulations as well as to assess any potential trade-off between advances in ICE technology towards increased efficiency and emissions. The consortium consists of European and US organizations, which are leaders in the field of aerosol and particle technology.

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1 Principle of Operation

CPCs are one of the most used instruments in aerosol science [1] for particle concentration measuring. Commercial CPCs provide the total number of particles, without size classification. The sizing feature is implemented by placing a DMA before the CPC, where the probability of ionization and the charge state of the particles need to be known for the size distribution to be inferred. The idea of a standalone CPC with sizing features dates back to 2000 [2], however, limited research has been done, with not enough success to be protected by patents.

The concept of the S-CPC is revolutionary, but the maturity of the technology is rather low. CPC counting is achieved by growing the particles of interest to optically detectable sizes via condensation of a supersaturated vapor on the original particles. This growth takes place above a size-dependent critical value S^* of the vapor saturation ratio (S) **Error! Reference source not found.**,

$$S = \frac{P}{P_v(T)} = S^*\left(d_p\right) \tag{1}$$

where, P, P_v, T and d_p are the partial pressure of the vapor, its equilibrium vapor pressure, the local temperature T and the particle diameter. Accordingly, the size of a certain particle can be determined by passing it through a supersaturated vapor of increasing S, until it reaches the critical value beyond which the particles grow into visible drops and may be counted. For a given population of particles, the size distribution can be inferred by passing it through a CPC of variable supersaturation, and measuring the number of particles N grown to visible sizes as a function of S, whence $N(S(d_p))$ is the cumulative size distribution.

The Turbulent Mixing Sizing CPC is based on the turbulent mixing between a cooled aerosol flow (containing the particles to be counted) and a hot gas saturated ($S=1$) with a low diffusion vapor. The mixing takes place in the mixing chamber, resulting in a flow with a uniform profile of vapor concentration and a temperature between the adiabatic mixture temperature and the temperature of the saturator walls. The turbulent mixing is achieved by the collision of two jets of aerosol flow with a high Reynolds number together with a jet of hot saturated gas.

After the mixing chamber, the flow is cooled by means of passing through a condensation tube with a constant temperature in the walls. The reason why the instrument needs a low diffusion vapor is to assure that the concentration boundary layer grows much slower than the temperature boundary layer. If this condition is met, the gas in the axis of the tube will reach the temperature of the wall before the concentration in the axis is affected by the contour condition of $S=1$ in the walls of the tube. Given these conditions, every point inside the condensation tube should have reached the desired S^* (at least a little time, enough to nucleate all the particles with $d_p>=d_p(S^*)$ in this point) in each step of the supersaturation sweep. The supersaturation sweep is carried out by varying the hot saturated gas flow rate at a given flow rate step. The difference between the temperature of the hot saturated gas and the temperature of the condenser wall, and the difference between the aerosol flow rate and the hot saturated gas flow rate determines S^*.

The problem is that by using a lowly diffusion vapor the nucleated seeds need a lot of residence time in the condenser tube to grow to optically detectable sizes. To accelerate the process, the flow is mixed with a flow of N_2, saturated with ethanol at room temperature. Afterwards, the mixture is cooled in a diverging condenser tube with constant temperature in the walls. To reach the wall temperature in the axis is not a key point in this second condenser (booster condenser) because the seeds are already nucleated. The only important condition is that the supersaturation must be higher than 1 so that the seeds grow to optically detectable sizes and lower than the S^* of the largest particle detectable by the instrument, in order to avoid

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nucleation at the booster. Finally, the flow enters in an optical particle counter capable of counting particles in flows with a high concentration of particles.

2 Innovation

Initially (March 2017), two design concepts were selected: (i) a steady adiabatic expansion S-CPC and (ii) a turbulent mixing S-CPC. After evaluating the strengths and weaknesses of both designs, the former was discarded in favour of the second variant, essentially because of the complexity of the fluid dynamics in the adiabatic expansion design and the good precedents of the turbulent mixing found by Gamero-Castaño and Fernández de la Mora [2]. A detailed description of this concept is shown in Section 3.

There are two key factors to achieve a good performance. First, a uniform temperature is required in the nucleator. Since this element is at a lower temperature than its vapor feedings (whose temperature cannot decay between the saturator and the nucleator to avoid vapor condensation, and hence artifacts), isolation between the saturator and the nucleator are critical. The nucleator was designed in cooper (high thermal conductivity, thus low temperature gradients) isolated between by PEEK plastic and air chambers. Peltier modules were used to cool the nucleator below room temperature. The other key factor is that the residence time must be high enough to allow the particles to grow up to visible sizes, but also as low as possible for high frequency measurements. In order to optimize the design for such goal, Computational Fluid Dynamics (CFD) was used. Figure 1 shows a temperature plot of the nucleator optimized design.

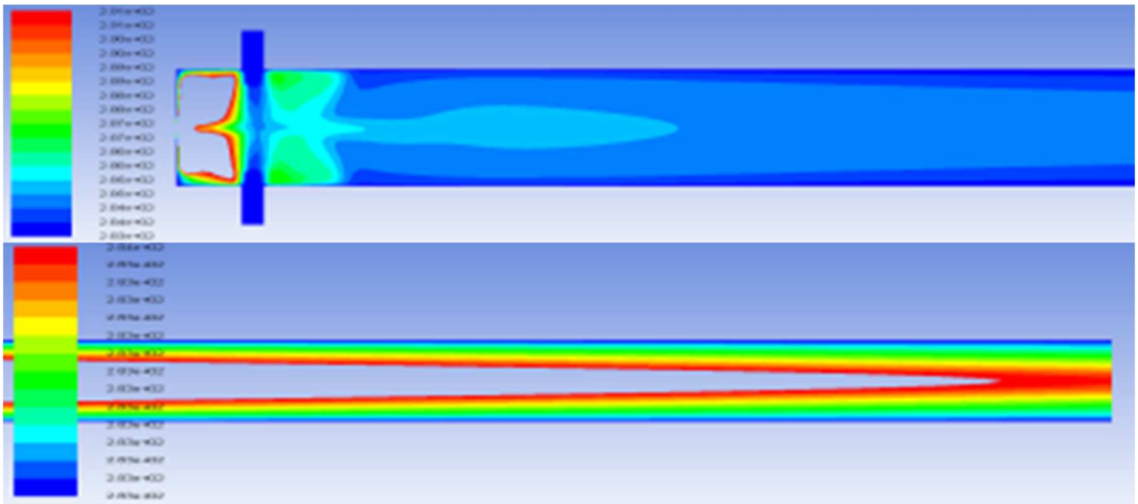

Figure 1 Temperature profiles. Top: temperature at the turbulent mixing chamber and nucleator inlet; Bottom: temperature at the nucleator outlet

Figure 2 shows a diagram of the first prototype. The first S-CPC prototype is housed in a box of dimensions 50x30x30 cm, and its temperature and fluid control modules take up a space of 30x30x20 cm each one. Power consumption is around 100 W.

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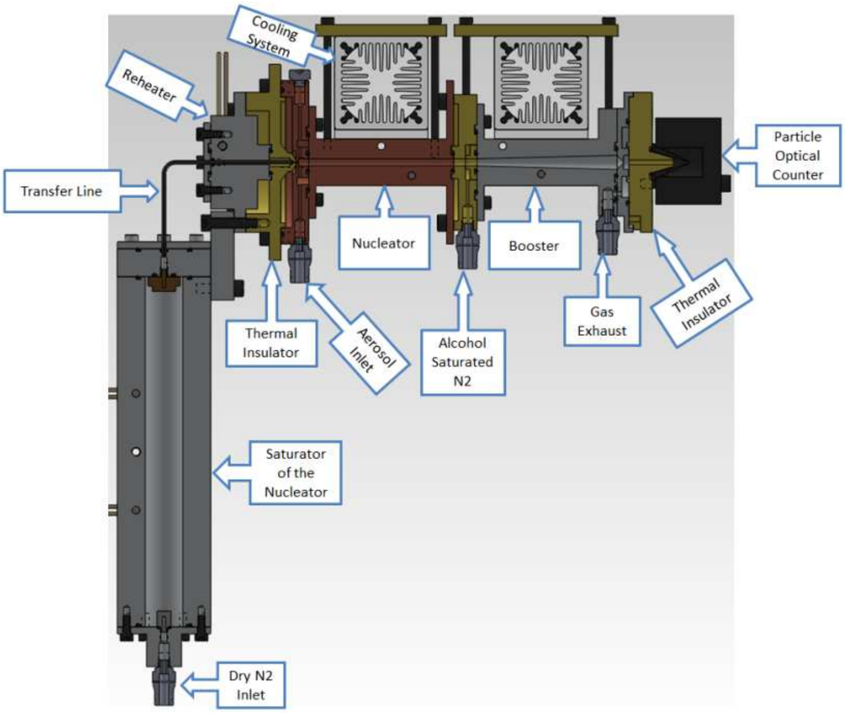

Figure 2 S-CPC design diagram

Automatization was also important, as the stabilization and synchronization of flow rates in order to change the supersaturation state of the condensing vapor is impractical if attempted with manual control. Furthermore, the parameters of PID (Proportional, Integral and Derivative) controllers had to be optimized. Such complex system needed novel control software and electronics, which also allowed tandem operation with DMA (required for the validation and evaluation test bench). Figure 3 shows the graphical user interface of the control software.

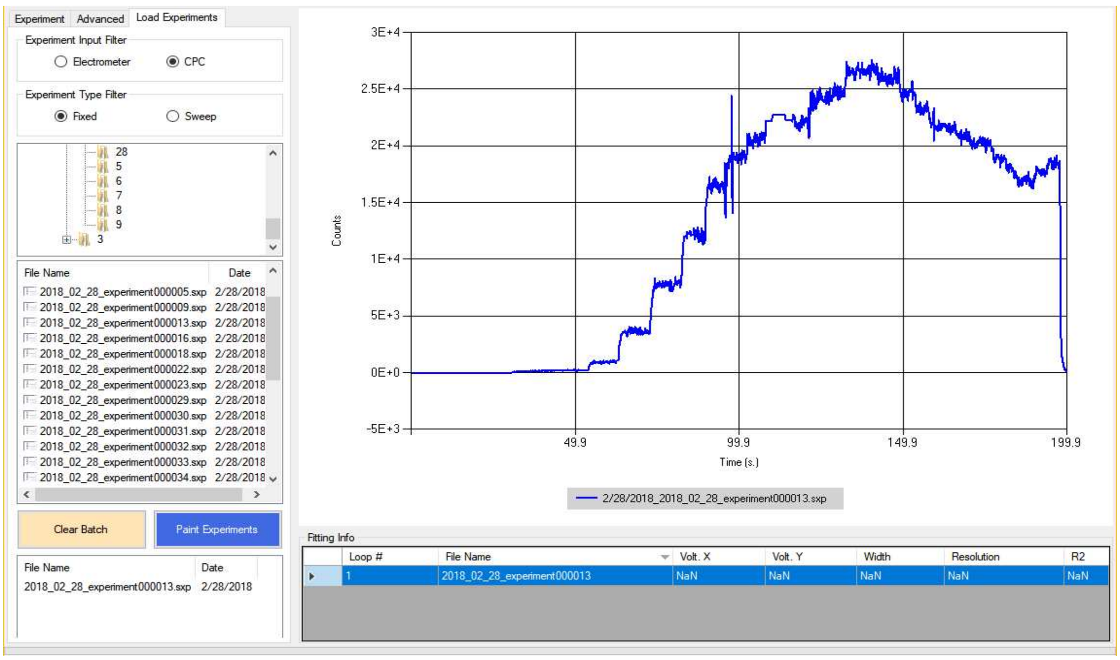

Figure 3 S-CPC control software

Once completed the design in July 2017, Implementation started in September 2017. Nearly before end of 2017, the S-CPC achieved conventional CPC performance and limited sizing performance. Research in order to select the most suitable condensing vapors for optimized sizing performance goes on.

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3 Modules and Integration

The test bench for the S-CPC is shown in Figure 4 and Figure 5. A bipolar electrospray chamber [3] was used as a, monocharged particle generator. Then, the polydisperse aerosol generated was turned into a monodisperse sample by means of a HM-DMA [4-5] and diverted to the S-CPC, in parallel with a Faraday cup electrometer [6] for comparison (see Figure 4).

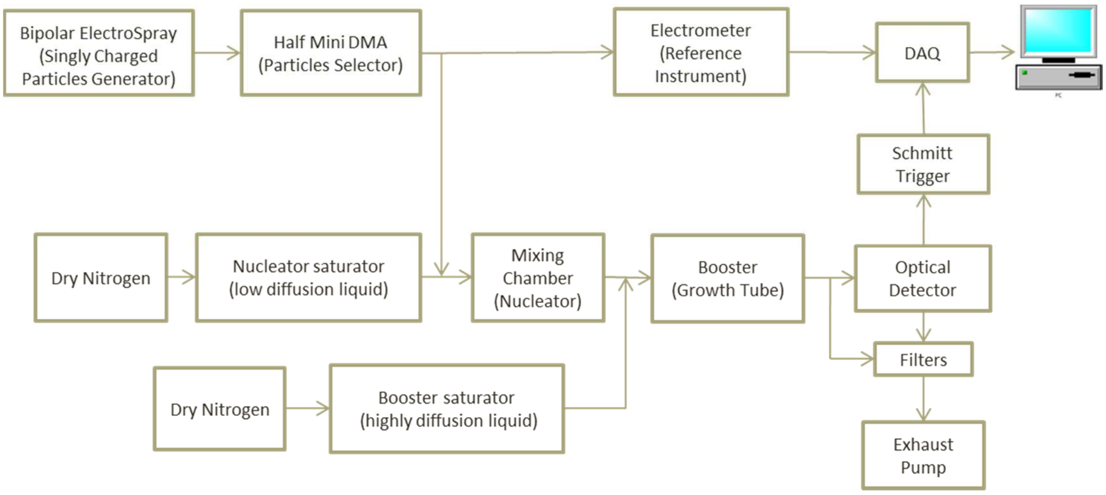

Figure 4 S-CPC test bench diagram

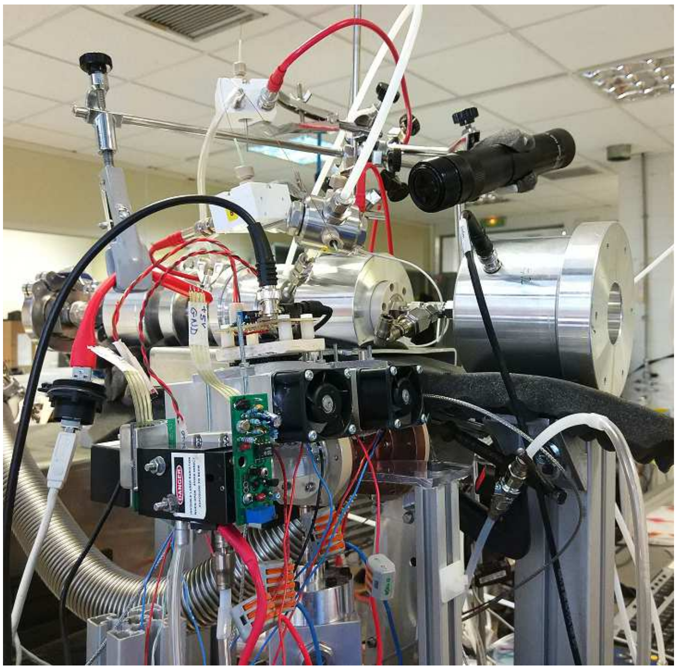

Figure 5 S-CPC test bench

Both the data from the electrometer and the S-CPC are acquired using the same Data Acquisition (DAQ) Card which allows the real comparison of the data in real time.

Having all the parameters of the S-CPC controlled is essential; hence, some control modules were designed, manufactured and validated in SEADM's laboratory. These modules can be grouped as follows: i) the heating control module to control the temperatures in the saturator of the nucleator, in the transfer line, in the reheater and in the saturator of the booster; ii) the cooling control module for controlling the Peltier system for the temperature in the nucleator and in the booster tube; and iii) the fluid control module for the fluid parameters in the instrument, this

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module is based on a digital microprocessor where some control routines are programmed for controlling the following variables: flow rate of the saturator of the nucleator, pressure of the saturator of the nucleator, sample flow rate, flow rate of the saturator of the booster, exhaust flow rate, output pressure and the optical detector's flow rate. The S-CPC also requires some software for creating an interface with the operator which helps in the data interpretation and the parameter controlling and monitoring. (Figure 6)

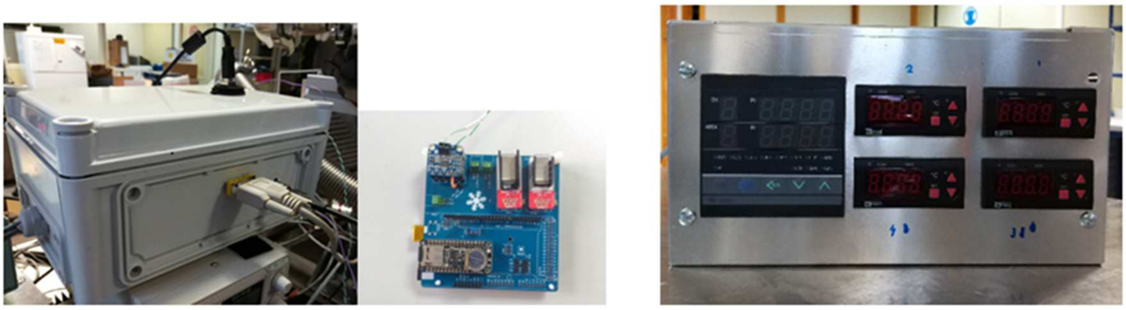

Figure 6 S-CPC Control modules: from left to right: optical detector and flows; Peltier system; heating

Figure 7 (left) represents one of the main screens of a current version of the software, developed in order to create different kind of experiments, represent them in real time, register the results of the experiments and facilitate the post-process of all the information obtained during the experiments. Figure 7 (right) represents software developed for controlling and data-logging the different flows, especially during the experiments, called Cpc Monitor.

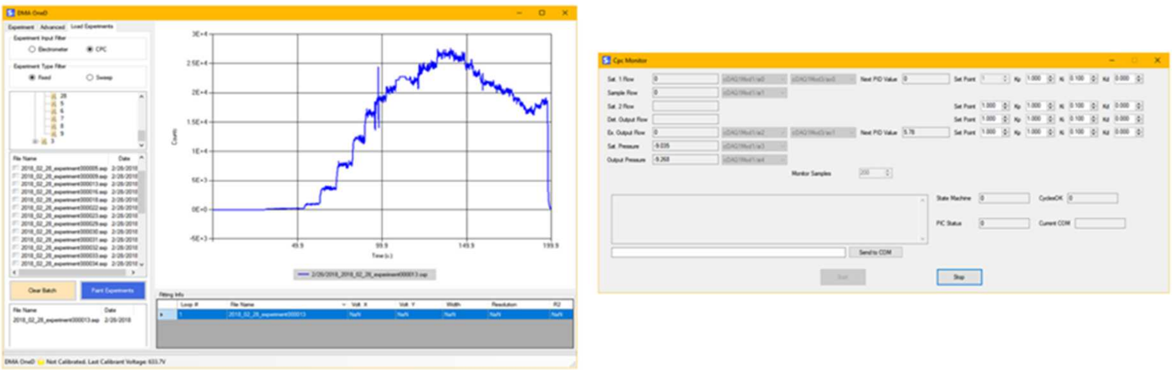

Figure 7 S-CPC software. Left: main user interface; Right: Data-logging

Given that the simultaneous control of two different software programs during the experiments by the operator is a complicated task, both programs were merged into one in the second version of the software, and certain tasks were automated (in particular, the sweeping of the saturator flow rate, during the experiments). This feature also helped to merge the output data of the experiments, which is especially useful at the time of post-processing the experiments. Additionally, as some actions were automated, the probability of committing an error by the operator during the performance of experiments is reduced.

The software allows the operator to create experiments that simultaneously control a Half-Mini connected to an Electrometer and the S-CPC, in order to simplify the S-CPC calibration, while verifying its correct operation.

The operator can create different kind of experiments, for example:

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- Fixing a unique voltage in the Half-Mini while fixing the saturator flow in the S-CPC.
- Fixing a unique voltage in the Half-Mini while sweeping the saturator flow in the S-CPC.
- Sweeping voltage in the Half-Mini while fixing the saturator flow in the S-CPC.
- Sweeping voltage in the Half-Mini while sweeping the saturator flow in the S-CPC, in a synchronized way.

The result of the experiments (electrometer signal, counts detected by the S-CPC) are saved in Text Plain Format (.txt), Excel Format (.xls) and in SEADM proprietary Format (.sxp), used by this software, or future SEADM applications, especially for post-processing functions. Also, the software was development for helping in the interpretation tasks, plotting the experiments chosen by the operator in the same graph. This functionality makes easier the analysis of the evolution of the different experiments during a laboratory session.

After the completion of all the required submodules and their individual testing, the integration of the first prototype was carried out in the laboratory. Setting up the first S-CPC was more challenging than expected due to the following reasons: some mistakes were detected from the manufacturing process, some improvements were proposed from the original design because the first versions and some parts were worn due to the individual tests previous the integration.

Also, the parts working with liquids required redesign to prevent flooding or oversaturation in the saturators. A reservoir was implemented between the booster and the detector to solve the flooding, while the oversaturation was solved by including silica gel. Other difficult challenges faced included automatization and stabilization of the fluids control, whose parameters had to be tuned empirically, and the compatibility of the Schmitt Trigger with the optical detector, which required a detailed study of the optical detector electronics. However, all of the problems faced could be solved by re-engineering the prototype and no physical barriers limiting the capabilities of the system were found.

4 Preliminary tests

First tests were aimed as a proof-of-concept. Ethanol was selected as nucleating vapor, and $[THA^{+}]_{n+1}Br_{n}$ clusters as particles of interest. The HM-DMA was set to provide a particle size of 7.5 nm. Figure 8 shows the activation of these particles. The red graph on the left side represents the S-CPC signal versus time. Each of the four steps represents a different supersaturation condition. The signal reaches a maximum when all 7.5 nm are grown to detectable sizes. In Figure 8 the blue graph on the right side shows the theoretical supersaturation values (based on the initial vapor content at the cold wall temperature) vs the normalized signal for each step.

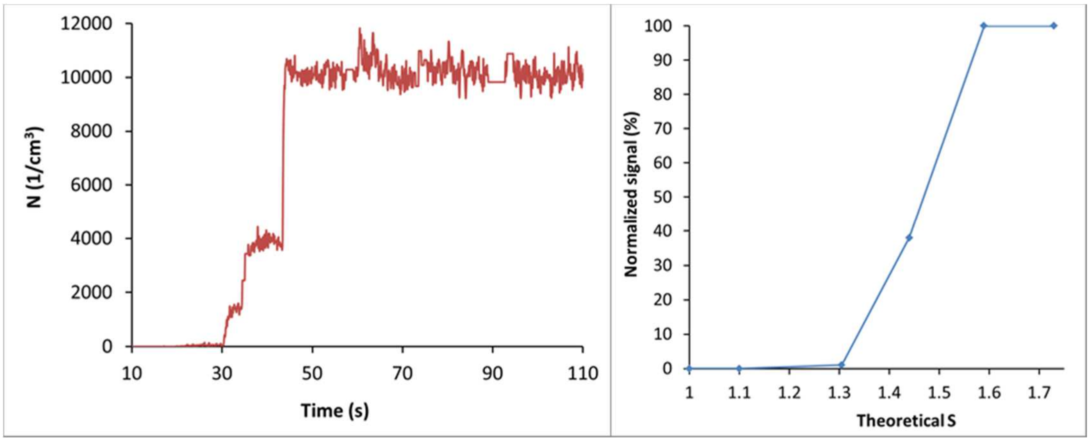

Figure 8 Left: Particle counting vs time, varying S. Right Theoretical S vs mean, normalized signal.

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Some results were obtained with this first version of the prototype, but the particle activations did not follow a constant distribution, the level of supersaturation, where the activation curve started, varied during the experiments, which indicates that some parameters were not well controlled such as the temperature, pressure or flow rates. Also some small leaks were detected which can generate changes in the gas conditions inside the instrument and some particles from the laboratory could go into the S-CPC, because the system works under atmospheric pressure, and they can modify the results.

After these results, we can conclude that the technology has been validated in lab (TRL4). The results are in line with the expected activation curves, the particles with one specific size are activated at one specific level of S-CPC (always higher than 1, supersaturation). The selection of the optimum saturator fluid will be based on the resolution, measured as the verticality of the activation curve, but before injecting different solvents, some other tests have to be performed such as repeatability, stability of the signal, background analysis, etc.

Some modifications of the second version of the S-CPC prototype are described below, taking advantage of the knowledge acquired by the first version design and testing.

• New design which avoids leakage problems. Solving this problem is essential for two reasons: Firstly, the fluid conditions inside the instrument have to be very well controlled as pressure and temperature variations highly affects the vapour supersaturation value. Secondly, in case of leak, some atmosphere particles could enter the system, being detected by the optical counter and faking the actual measurement.

• Transfer line insulation and heating enhancement. It is needed to insulate the transfer line between the saturator bloke and the CPC mixing chamber in order to ensure that there is not a temperature gradient and condensation in the transfer line.

• Reheater redesign to avoid condensation issues and blocking problems before the turbulent mixing chamber, as originally, the tip of the capillary was not heated in the mixing chamber entrance. This issue generated the same problems as the lack of the capillary insulation, so the reheater part needed to be modified in order to coat more surface of the capillary.

• Modification of the mixing chamber part. It was needed to modify the geometry of the mixing chamber peek part as a problem related with the capillary was founded. The problem was that there was no self-centering geometry and the bad alignment of the two parts modifies the gas conditions in some parts of the S-CPC.

• New precise cooling temperature system. As it has been explained before, the control of the temperature and pressure conditions is essential to guarantee a right nucleation and drop growing. Hence, an enhancement in the temperature control was needed in order to have a good control under different atmospheric conditions.

• New precise and automatic fluid control. There has been an implementation of an automatic system that controls the saturator flow through a DAQ (Data AcQuisition), that allow the system to rapidly ramp the saturator flow from 0 to 500 mililiter per minute (mlpmin).

• Optimization of the Schmitt Trigger of the Optical Detector.

• New software with a logging and monitoring of all parameters. The new software allows observing the sampling particles intensity what highly helps to understand and evaluate the quality of the results obtained during the testing and calibration. There were also other improvements, like showing in the screen the different temperatures, the system pressure or the flow values in real time. Moreover, there was included a post-processing tool that allowed to show the particle counting detected vs flow rates instead of time, as it was before.

• New filling system of the saturator in order to avoid flooding problems. As there is a need to work with chemical solvents, it was needed to implement a new refilling method which allows

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to safely refill the saturator solvent and to more precisely control the liquid consumption in the saturator.

Some of the activities are already completed and installed.

The second version of the prototype is almost completed and a testing plan is already defined with the aim of completing the first unit of the second version at the end of June. As soon as the first results are obtained, the development of the PEMS (Portable Emissions Measurement System) will start.

5 CONCLUSIONS

The S-CPC development was quite challenging and time-consuming, but it is expected to meet the requirements of the project. After a thorough technical study, the decision of selecting the turbulent mixing as the final solution for SUREAL-23 project was taken. The first version of the turbulent mixing S-CPC was designed and simulated at M12 and it was manufactured at M18. This first prototype achieved conventional CPC performance while the optimization of the sizing performance continues. Testing of the instrument on real engine exhaust will follow with the contribution the SUREAL-23 partners. A second version of the prototype is under manufacturing and it will be tested also in SEADM and then to the other partners facilities.

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