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# Understanding and Measuring Sub-23 nm Particle Emissions from Direct Injection Engines

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**Abstract**

A large fraction of the total number of particles emitted by direct injection engines are below the adopted 23 nm diameter threshold and although the EU aims to regulate these emissions, this is not yet possible due to the absence of accurate and reliable quantification methods, especially under real driving conditions. Four research organisations, three particle measurement instrumentation companies and one automotive OEM have joined forces in the framework of the EU-funded project SUREAL-23 to overcome such barriers by introducing novel technology for the measurement of sub-23 nm exhaust particle concentration, size and composition. The main objectives of SUREAL-23 are to (a) simplify and make more robust the exhaust aerosol sample treatment, (b) elucidate the effect of different diesel and gasoline engine operating conditions on sub-23 nm particle emissions and (c) advance particle measurement technology with the introduction of novel techniques. Herein, we present our latest efforts on instrumentation development and aerosol sampling.

*Keywords:* Sub-23 nm particle emissions; nanoparticle measurements; Environmental Impact of Transport.

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**Nomenclature**

| | |
|---|---|
| CAST | Combustion Aerosol Standard |
| CPC | Condensation Particle Counter |
| CS | Catalytic Stripper |
| C40 | Tetracontane |
| DR | Dilution Ratio |
| EU | European Union |
| GDI | Gasoline Direct Injection |
| HM-DMA | Half Mini Differential Mobility Analyzer |
| IC | Internal Combustion |
| ICAD | Induced Charge Aerosol Detector |
| OEM | Original Equipment Manufacturer |
| PEMS | Portable Emissions Measurement System |
| PMP | Particle Measurement Programme |
| PN | Particle Number |
| PNC | Particle Number Counter |
| SMPS | Scanning Mobility Particle Sizer |
| TGA | Thermogravimetric Analysis |
| VPR | Volatile Particle Remover |
| WHO | World Health Organization |

## 1. Introduction

Vehicles powered by direct injection engines, both Diesel and GDI, are considered a primary source of ambient particle related pollution with impact on climate change (Menon et al., 2002) and severe adverse effects on public health (Alföldy et al., 2009). In June 2012, WHO confirmed the toxicity of diesel particulates and classified them as a "group 1: definitely carcinogenic to human beings" harmful substance. Adverse health effects from vehicle emissions drove many countries, on both sides of the Atlantic, to introduce emission limits. In Europe, emission limits were initially introduced on the basis of emitted particulate mass (Euro 1 to Euro 4). Numerous studies showed that ultrafine particles, with no significant contribution to total emitted mass, are more hazardous on a per mass basis to human health than bigger particles (Ferin et al., 1992) and pushed European legislative authorities to complement the particle emission limits with a solid particle number concentration limit, with a particle size cut-off at 23nm in Euro 5b for Diesel and in Euro 6 for GDI engines.

The total emitted particle number is highly variable due to internal (*e.g.* coagulation) and external (*e.g.* diffusion) processes (Friedlander, 2000). Thus, its use as a basis for regulation necessitates a robust sampling and measurement method that permits reproducible and comparable experimental results. In Europe, this initiative was led by the PMP, which after many years of experimental campaigns and inter-laboratory data analysis proposed a solid particle number measurement method, also known as the PMP protocol (Martini et al., 2009). Accordingly, the raw exhaust is driven to a full flow dilution tunnel utilising a constant volume sampling. Possible volatile and semi-volatile material that condenses on solid particles or creates a separate nucleation mode is evaporated in a VPR and then particle number is measured by a particle number counter having a size cut-off at 23 nm. The VPR consists of two dilution stages: a first stage using hot dilution air, to suppress condensation and/or droplet nucleation, and a second with cold dilution air, to lower the sample temperature. An evaporation tube is inserted between these dilution stages to bring any already condensed volatile components back to the gas phase. The first dilution stage must reduce the volatile concentration to the extent that condensation and re-nucleation after the evaporation tube are improbable when cold dilution reduces the sample temperature.

One of the problems identified with the standard sampling procedures is the potential formation of particles in the sub-23 nm region, the so-called artefacts, despite the dilution applied, by pyrolysis of hydrocarbon-derived precursors and sulfuric acid re-nucleation (Swanson and Kittelson, 2010). Although the formation mechanism is not entirely understood, the outcome is the production of spurious particle populations that are not present in the exhaust gas. Since current regulation limits the measured particles from 23 nm and above, this does not affect the

compliance-relevant PM concentrations. Difficulties in introducing a robust measurement protocol in this particle size range of currently available technologies led regulation authorities to ignore their contribution to ambient pollution.

Fushimi et al. (2011) report that particles in the 10-30 nm size range, regarding composition, may be solid (amorphous or graphitised carbon, metals etc) or liquid (hydrocarbons and sulphur species). According to the insightful review of Giechaskiel and Martini (2014) on engine exhaust sub-23 nm solid particles, the GDI-emitted sub-23 nm solid particle fraction is around 40% while for diesel engines it is 20%. In light of the changing engine technology landscape and the focus on vehicle emissions, mainly due to evolution in engine and exhaust after-treatment technology, the need to measure below the currently enforced 23 nm cut-off in particle size is now well established. Further, better measurement and understanding of these sub-23 nm exhaust particles will also benefit fuel, IC engine and emission control development efforts.

SUREAL-23 is an EU-funded project that endeavours to investigate in detail the sub-23 nm solid particles emitted by direct injection engines. Starting from October 2016, SUREAL-23 is hosting numerous efforts to:

- Develop new instrumentation to complement standard PMP and extend the available analytical toolset, by providing transient PN measurement as well as size and composition classification specifically for the sub-23 nm size region, while pursuing the reduction/elimination of requirements for exhaust sample conditioning by applying high-temperature operation instruments.
- Provide a simple and robust exhaust aerosol sample treatment with increased volatile material removal efficiency and minimal particle losses.
- Investigate the effect of different diesel and gasoline engine operating conditions (fuel additives, bio-content, gas fuel addition, after-treatment type and operation, etc.) on sub-23 nm particle emissions
- Integrate the most suitable components of the extended sub-23 nm measurement toolset proposed developments into PEMS and verify their measurement capability in real driving conditions.

Herein, we present preliminary results derived from the first year of the SUREAL-23 Project, including developments in instrumentation, aerosol sampling and conditioning, which have provided some first conclusions and proposals for future investigations.

## 2. Advanced aerosol measurement technology

PMP-standard exhaust particle instrumentation requires sample temperature conditioning to avoid damage or abnormal operation and therefore is not suitable for measuring directly from the exhaust tailpipe, i.e. dilution and cooling of the exhaust gas sample is required. The outcome of the sample conditioning process is path-dependent due to the presence of volatile substances that may condense on existing solid particles or nucleate as new ones as the sample temperature is lowered. Particularly for the sub-23 nm range, the sampling can have a major effect on the particle properties and parameters to be measured. SUREAL-23 intends to face the above-described difficulties by developing aerosol measurement technologies with reduced sampling/treatment requirements by providing the means to measure at higher final sample temperatures. Lower overall dilution is also sought to achieve sub-23 nm particle sample concentrations sufficient for reliable size-specific characterisation.

### *2.1. The Advanced Half-mini DMA*

The HM-DMA system (Fig. 1a) is a supercritical DMA, with a 2 cm working section, initially developed at Yale University and subsequently improved by SEADM (Boecillo, Spain) able to classify aerosol particles (including molecular ions) in the size range 1-30 nm with high resolution (Fernandez de la Mora, 2017(1)) and fast acquisition frequency (Fernandez de la Mora, 2017(2)). The working principle involves particle ionisation (unipolar charging) by a secondary electro-spray and classification under the simultaneous action of the well-controlled axial sheath flow and a strong radial electric field, whereby only the particles of a specific mobility are transmitted to the DMA outlet. The main novelty of the system consists in its ability to maintain a laminar flow even in the presence of high sheath flow rate which is necessary for classifying particles with high resolution in the particle size range of interest. Innovative geometry is used to avoid diffusion broadening and turbulence-related effects. Also, a significant feature is that it can accommodate hot sampling by employing a heat-tolerant semiconducting glass tube in the path from the inner electrode to the grounded outlet of the DMA, yielding a device capable of operating at temperatures up to 200 °C. By eliminating the need for high sample treatment (i.e. PMP system), known artefact creation mechanisms are avoided resulting in more reliable solid particle emission

measurements. Furthermore, HM-DMA offers the option of detecting both positively and negatively charged particles (e.g. the natural charge distribution of the exhaust particles when the electrospray is not active), providing an even additional insight on the nature of the combustion aerosols considered.

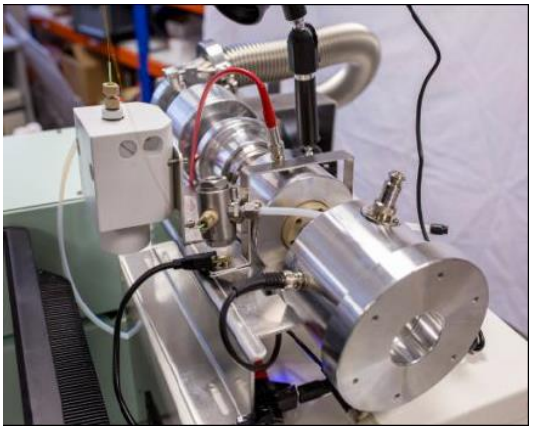
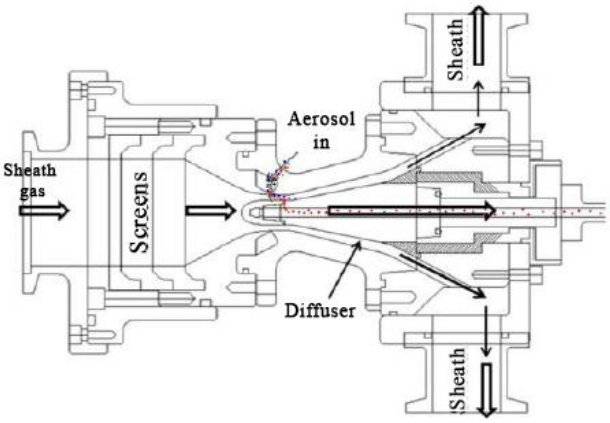
a  b 


Fig. 1 a) Schematic of the working principle of HM-DMA; b) Picture of a HM-DMA unit

The system was tested against ultra-fine reference aerosols produced by (a) a CAST® burner, a well-established standard aerosol generator, widely used for calibration purposes of concentration and size measurement devices and (b) a commercial power generator running on Diesel fuel with a Ce-based additive. In the current work, the CAST burner was used to obtain aerosols with non-standard but repeatable characteristics regarding concentration, size distribution, structure and organic fraction of the nanoparticles, by modifying the relative flow rates of the fuel/oxidation/quenching gas mix that govern its diffusion flame combustion. The Ce-additive was employed in the Diesel fuel to produce ultra-fine particles. As reported in the literature (Giechaskiel and Martini, 2014), addition of fuel additives may result in a separate solid nucleation peak.

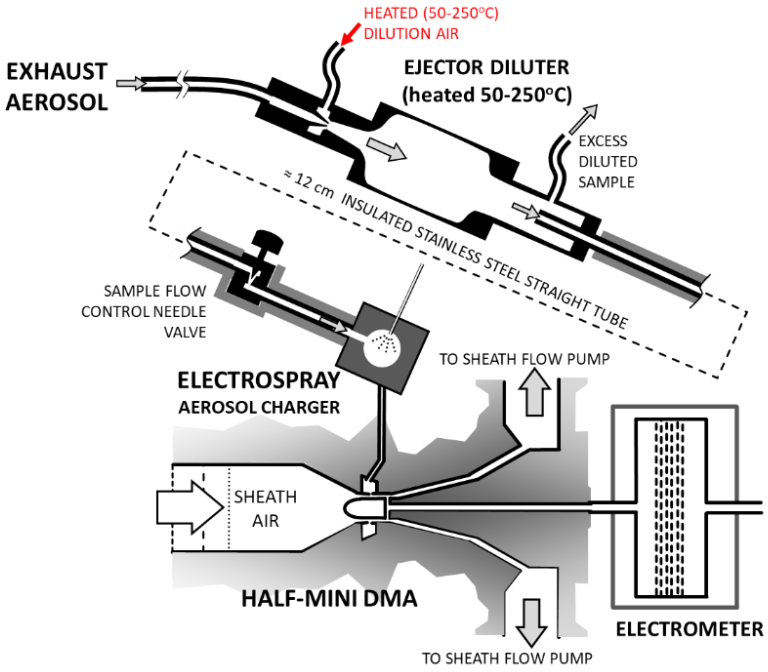



Fig. 2 Setup for measurements with the HM-DMA measurements setup with CAST aerosol

As a reference aerosol, CAST critical flows ($C_3H_8$, Air, $N_2$) were appropriately adjusted to generate an aerosol which we designated as "M10" (nominal particle diameter of 10 nm), which was well characterised in a recent study (Daskalos et al., 2017). In more detail, when the aerosol M10 was measured with an SMPS (TSI®

3080/3085/3776) the mean diameter ($d_m$) of the nanoparticles was estimated at ~10nm, while TGA (Pyris® 6) revealed a large volatile component, estimating the organic fraction to be in the range of 50 w/w% . When the same analysis applied to the particle emissions from the engine running on the Diesel fuel with the additive, solid ultrafine particles with average size of approximately 20 nm were demonstrated. In both cases (CAST and engine) the exhaust sample was acquired by an ejector-type diluter with heating capability up to 250 ºC and a dilution ratio of about 10. Part of the diluter's outlet flow is guided into the electrospray chamber and subsequently into the DMA stage to be classified and finally into the electrometer to be detected as shown in Fig. 2.

We managed to operate the HM-DMA reliably in combination to both exhausts with good reliability. Fig. 3 shows CAST exhaust measurements displaying a mean particle diameter of 8-9 nm for the M10. It has to be noted that at the lower size range (1-4nm) clusters of peaks also existed, but these are omitted from the graphs as they should be attributed to impurities in the electrospray solution (ionised clusters/droplets of the non-volatile impurities) and not to exhaust particles.

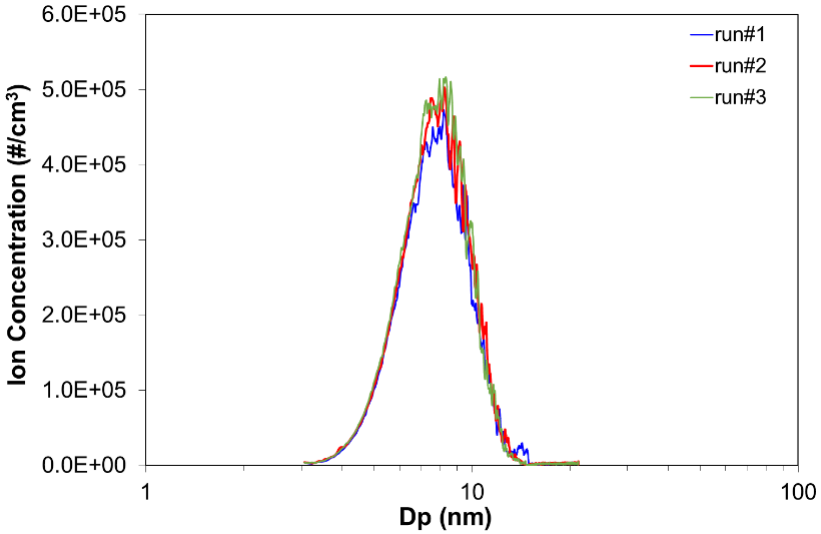



Fig. 3 HM-DMA repeatability assessment graphs for a) Cold Operation and b) Hot Operation

Fig. 4 presents a comparison between measurements with the HM-DMA operating at two different temperatures: 50 ºC and 160 ºC. The difference in the two curves could be attributed to the volatile nature of the M10 CAST particles. When operating at hot conditions volatiles are evaporated and are not counted by the HM-DMA, thus be varying the instrument's operating temperature one could simply characterise the nature of sub-23 nm particles for their volatile content.

Fig. 5 presents measurements at the engine exhaust. HM-DMA results are presented in comparison to SMPS results at the same engine operating conditions. The instruments use different sampling systems. The SMPS samples form a PMP compliant system with a dilution ratio of about 64 and an evaporation tube operating at 300 ºC. The HM-DMA draws the sample from the ejector-type diluter with no heating (T=50 ºC and dilution ratio = 10). As already mentioned, the ultra-fine particle emissions from the engine running with fuel additive have insignificant volatile content. The three curves presented in each graph correspond to different fuel additive amounts. An increase in the fuel additive causes an increase in particle total number concentration and a slight increase in the mean particle size as measured by both setups. It has to be noted that the particle classification provided by both instruments are quite similar although the SMPS is using the highly sophisticated PMP system and the HM-DMA measures with only one diluter at a small dilution ratio.

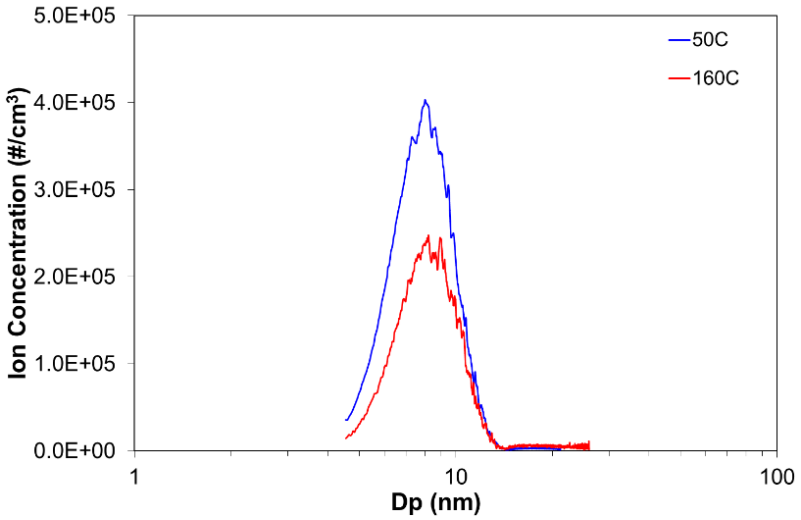



Fig. 4 Comparison of the average HM-DMA size distributions that resulted for different temperature levels

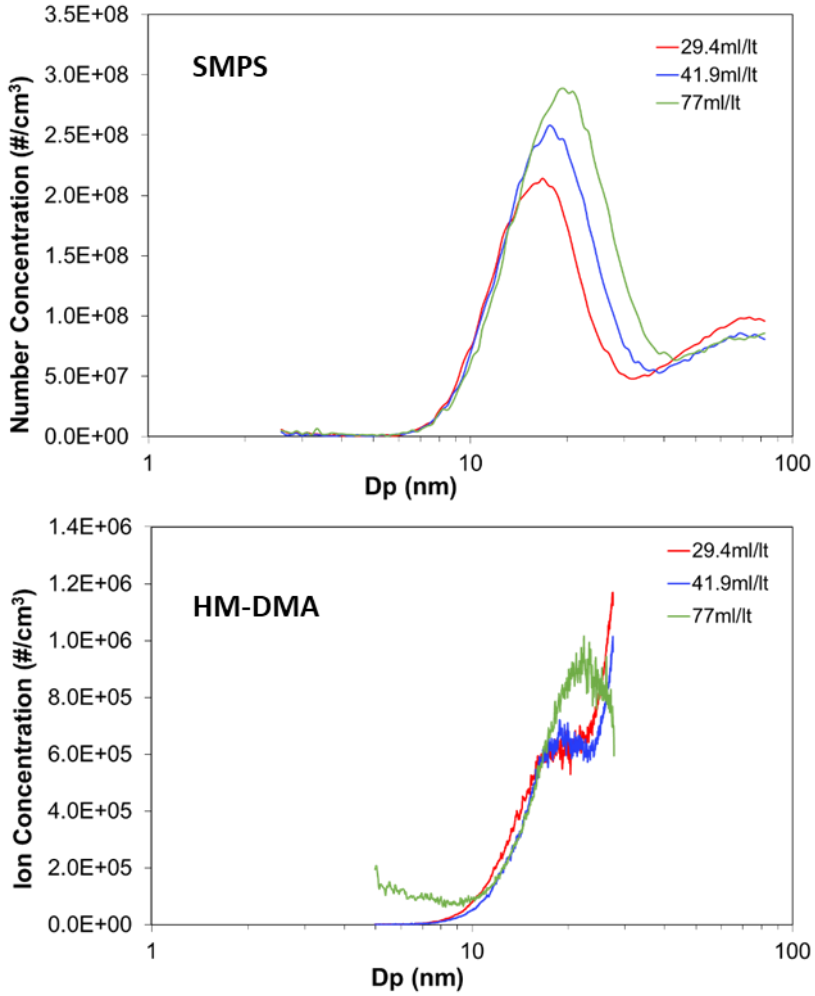



Fig. 5 *SMPS (top) and* HM-DMA *(bottom)* measurements on engine exhaust for three levels of fuel additive concentration.

### *2.2. The Advanced Induced Charge Aerosol Detector (ICAD)*

The ICAD is a concept derived from the induced current measuring principle recently developed by FHNW (Fierz et al., 2014) and marketed as the Automotive Partector by the FHNW spin-off Naneos Particle Solutions GmbH. The evolved automotive-applicable concept involves the addition of a pulsed electrostatic precipitator (see Fig. 6).

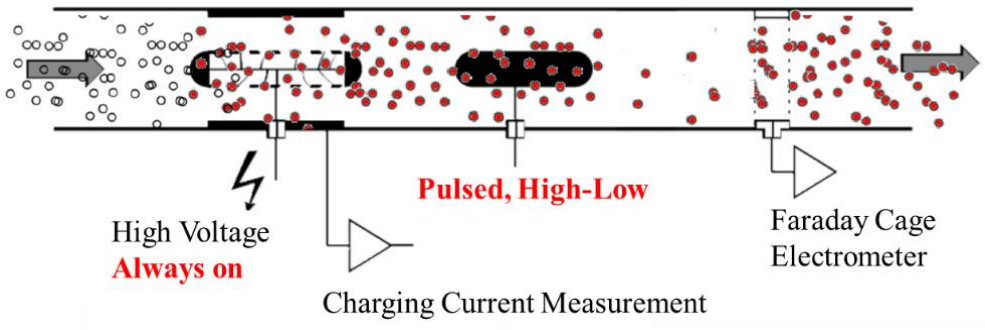



*Fig. 6* Measurement principal of ICAD

Some of the technical characteristics of the instrument include a response time of 1 sec, maximum particle concentration of $1.5\times10^6$ #/cm³ and a sampling flow rate of 2 LPM. The addition of the pulsed precipitator produces an instrument respond that can closely match the PN measurement response of the automotive CPC up to 200 nm. The initial design of the device had a cut-off particle size at 23 nm, to be in accordance with the EU legislation. For the scope of the SUREAL-23 project, it was necessary to include the ability to measure smaller particles. Several advances in the design have enhanced its operating temperature range and lowered the cut-off size to around 15 nm (see Fig. 7). The higher operating temperature range, currently up to 150°C, will allow the use of a much simpler sampling and conditioning system, with lower particle losses, especially in the particle diameter region of 10-23 nm. The small size of the instrument, overall robustness along with the non-demanding sampling system, provide a measurement setup suitable for PEMS.

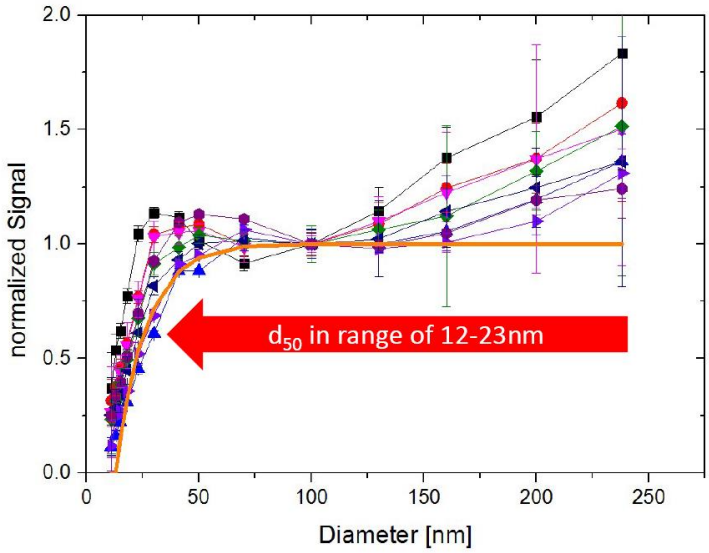



Fig. 7 Different settings in the ICAD lead to cut-offs below 23 nm

## 3. Aerosol sample treatment

Sub-23 nm particles measurement and, therefore, regulation, necessitates a rigorous sampling and conditioning technology able to deliver solid emitted particles with minimum particle losses. PMP-compliant VPR setups include a hot and a cold dilution stage combined with technologies that remove volatile particles; the evaporation tube, the thermo-denuder, and the catalytic stripper (Giechaskiel and Martini, 2014). Among these three technologies only the catalytic stripper seems currently able to comply with future limitations for sub-23 nm particles because both the evaporation tube and the thermo-denuder have been found to create artefacts that emanate from volatile material re-nucleation (Swanson and Kittelson, 2010).

Within SUREAL-23, a prototype sampling system was designed and constructed by APTL, in which the aerosol flow first passes through a hot porous tube diluter and then through an evaporation tube or a catalytic stripper. A downstream ejector diluter creates suction which drives the sampling glow and provides a further dilution. The whole system is fully integrated and flexible in terms of DR and temperature. This flexibility is advantageous

especially for the study of sub-23 nm particles nature but also for applying a unique sampling system for different instrumentation developed in SUREAL-23.

Catalytic strippers typically consist of monolithic flow-through reactors, primarily providing an oxidation catalyst to remove hydrocarbons, in some cases combined with a sulphur-trap. This technology was first introduced by Khalek and Kittelson (1995) who used a commercial DOC to oxidise hydrocarbons. For the catalytic stripper realisation in SUREAL-23 the following strategy was applied: initially, a number of high-temperature sorbents were synthesised and tested for their sulphur storage capacity. The most efficient of these materials were coated on ceramic honeycomb monoliths. Additionally, part of the monoliths was coated with a Pt-based coating in order to achieve high oxidation rates. Finally, the complete catalytic stripper was designed and constructed for high flow function that permits high exhaust particle penetration. The most efficient of the catalytic strippers tested consists of a dual-function cordierite monolith (diameter: 25.4 mm, length: 50 mm) coated with Ce/Zr/Pt. The operating wall temperature is $T_w$=400 °C, while the flow can vary up to a maximum of Q=25 LPM. The novel approach of a single dual-function monolithic reactor permits high-efficiency volatile material removal at minimum particle losses.

The catalytic stripper's oxidation efficiency was tested with tetracontane ($C_{40}H_{82}$) particles. According to the current legislation, the catalytic stripper should be able to oxidise with more than 99% efficiency $C_{40}H_{82}$ particles with 30nm diameter. $C_{40}H_{82}$ particles were generated with an APTL's prototype evaporation/condensation reactor and then passed through the catalytic stripper. The particle size distribution and the number concentration with and without the CS were measured with an SMPS (NanoDMA, TSI 3085, and CPC, TSI 3775) and a CPC, TSI 3775. The total $C_{40}H_{82}$ particle concentration was in the order of $10^6$ and the mean diameter ~30nm. Fig. 8a shows a typical $C_{40}H_{82}$ particle size distribution for Q=20 LPM, while Fig. 8b plots the CS oxidation efficiencies against the different flows tested. Current legislation is covered up to 25 LPM while possible future legislation for 99.9% $C_{40}H_{82}$ particles oxidation (Giechaskiel and Martini, 2014) is covered up to Q=20 LPM. Further experimental investigations will be performed for the CS's sulphur adsorption capacity and the solid particle penetration.

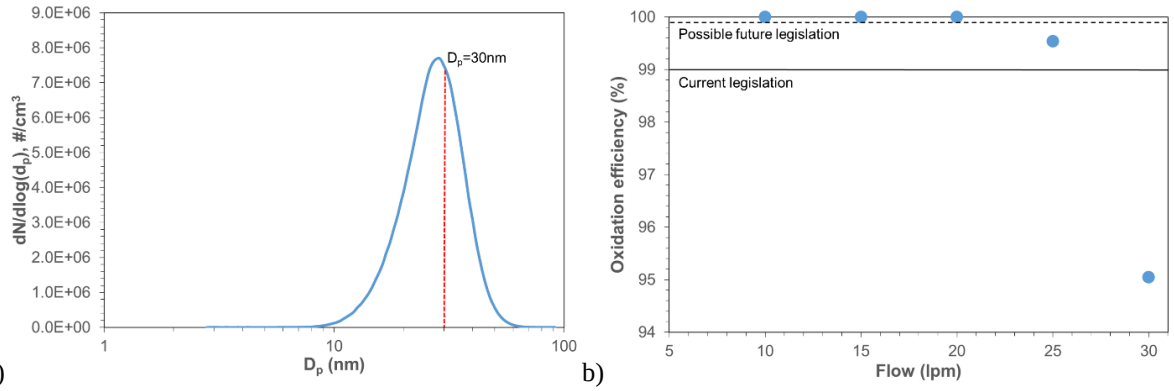



Fig. 8 a) C40 particle size distribution for aerosol flow 20 LPM; b) CS oxidation efficiencies for different aerosol flows at Tw=400C.

The sulphur storage capacity of the CS was tested with gaseous sulphur dioxide ($SO_2$). Specifically, a flow of 8 LPM containing 23 ppm $SO_2$ was passed through the CS. This concentration is much higher than the one expected at the exhaust of diesel and gasoline vehicles. However, inlet $SO_2$ concentration does not influence the catalyst performance (Limousy et al., 2003). An MRU Vario Plus gas analyser was placed downstream of the CS to measure the $SO_2$ concentration evolution. Fig. 9 plots the $SO_2$ concentration against time; initially, for a period of 840 s, $SO_2$ is totally adsorbed, while afterwards breakthrough gradually increases until outflow concentration matches that of the inlet. We define the catalyst total $SO_2$ adsorption capacity only for the first 840 s that $SO_2$ outlet is zero to avoid formation of artefacts. By integrating the area under the inlet concentration for the first 840 s we calculate the total $SO_2$ adsorption capacity of the CS which equals 3.5 mg or 0.27 g/L of catalyst volume.

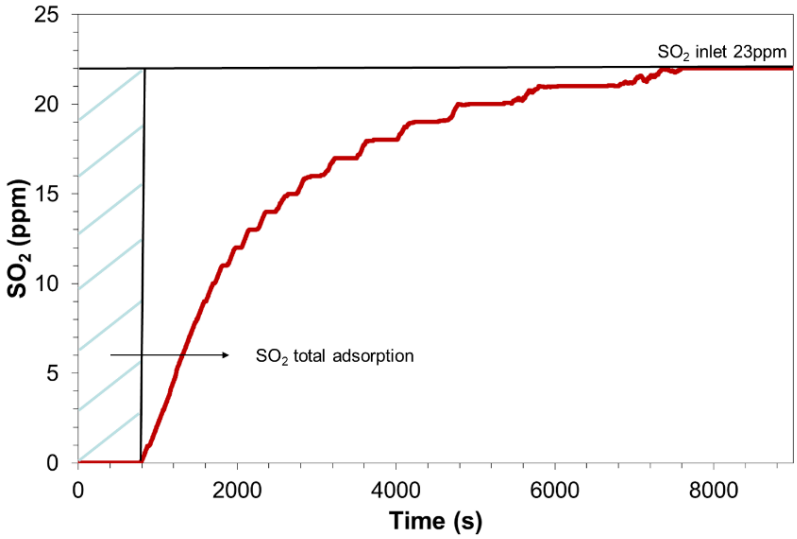



Fig. 9 $SO_2$ concentration downstream of the CS plotted against time.

## 4. Conclusions

The objective of our study was to present developments achieved in the EU-funded project SUREAL-23 for the robust measurement of sub-23 nm vehicle emitted particles. We presented two advanced measurement methods: a HM-DMA able to classify exhaust particles with high efficiency in the 1-30 nm size range at elevated temperatures (~180 °C) and an advanced charge-based particle counter (ICAD) with a reduced cut-off size at 15 nm and capable of operation at up to 150 °C. Higher temperature particle instrumentation expands the scope of exhaust particle characterisation while reducing particle losses and sample conditioning requirements. In additionally to instrumentation developments, the SUREAL-23 project is developing an integrated exhaust sampling/conditioning system incorporating a catalytic stripper optimised for the application at hand. Preliminary results show that the catalytic stripper's oxidation efficiency is compliant to PMP demands for exhaust sample flows up to 25 LPM.

Following on from the first year's achievements, SUREAL-23 will proceed with further measurement technology developments which will be used for an extensive characterisation of tail-pipe out particulate emissions of current and emerging direct injection IC engine powered vehicles. A photoacoustic sensor and a photoelectric ionisation concept will complement the mainstream instruments for particles characterisation by distinguishing exhaust aerosol composition. Additionally, a sizing CPC and a high-resolution DMA will be assessed for their compatibility and advantages in the characterisation of sub-23 nm exhaust particles. Following the instrumentation development, the effect of different diesel and gasoline engine operating conditions will be elucidated and, more specifically, studies will be performed on the effect of fuel additives, bio-fuel content, gas fuel addition and after-treatment devices on sub-23 nm particle emissions. Finally, the most suitable components of the extended sub-23 nm measurement toolset will be integrated into PEMS and particle emissions under real driving conditions will be examined.

## Acknowledgements

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