Portable Nano-Particle Emission Measurement System

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Publishable Executive Summary

This report concerns the current progress in the PEMs4Nano project towards discrimination of particles emitted by a generic single-cylinder test motor. Sampling of solid particulate matter was performed using various instruments, in order to develop the methodology best adapted to the test motor and to the analysis techniques used for particle characterisation. The size-dependent chemical composition of particles derived by analysis of samples from this campaign will be integrated into ongoing modelling activities to describe the particulate matter from motor to tailpipe, as well as informing future in-situ and ex-situ sampling campaigns.

One of the central pillars of Work Package 3 "Measurement integration into system development" is the derivation of a fundamental understanding of particle evolution from source to sampling point. The strategy applied to the achievement of this lofty goal is to combine physical measurements – ranging from in-situ monitoring of the particle size distribution using particle sizers (SMPS, EEPS) and optical characterisation (laser induced incandescence, LII) to the analysis of the chemical composition of particulate samples collected on substrates – with a sophisticated particle evolution model, taking into account both the modification of the particle size distribution due to physical processes such as agglomeration, but also the processes leading to the chemical distribution of particulate matter (including the categories "ash", aromatic carbon, metals, and sulfur-bearing compounds).

In particular, this report focuses on Task 3.1 "Particle characterization and evolution on single-cylinder engine". We will present the measurement strategy developed to collect particulate matter from the single-cylinder test engine at **BOSCH** under controlled conditions using various particle deposition instruments and various substrates. The results discussed in this report concern the second particle sampling campaign. The first campaign, described in detail in Deliverable **D2.3**, revealed the chemical composition of particulate matter collected on borosilicate filters based upon analyses performed at **ULL** and **HORJY**. There was no exploration of the parameter space of the engine working point, nor any size selection of particles, as the aim of the first campaign was to optimise analytical techniques at **ULL** and **HORJY** for the study of particulate matter from a gasoline motor. In the second particle sampling campaign, described in this report, the aims were more extensive. The sampling strategy employed for the second campaign was multi-fold, requiring the collection of size-selected particles (down to 10 nm) for analysis with mass spectrometric techniques (borosilicate and gold-coated silicon substrates), microscopic analysis (silicon substrates for scanning electron microscopy and copper grids for transmission electron microscopy), and combined spectroscopic-microscopic techniques (atomic force microscopy and tip-enhanced Raman spectroscopy).

Analytical techniques at **ULL** and **HORJY** are perfectly adapted to determining the surface chemical composition of particulate matter collected from the generic single-cylinder test engine at **BOSCH**. Two complementary mass spectroscopic techniques are available at **ULL**: Laser desorption Laser ionisation Mass Spectrometry (L2MS), developed in-house at **ULL**, and the commercially-available Secondary Ion Mass Spectrometry (SIMS). These techniques allow the analysis of the surface chemical composition of deposited particulate material by volatilisation and ionisation of surface molecules, which are distinguished and identified according to their mass using Time of Flight Mass Spectrometry (ToF-MS). The mass spectrometry techniques available at **ULL** are especially well adapted to the identification of hydrocarbon species (including polycyclic aromatic hydrocarbons (PAHs) and substituted hydrocarbons), metal species (from the fuel, lubricating oil, or engine wear), and sulfur-containing species (very important for modelling particle growth mechanisms). Atomic force microscopy (AFM) is performed at **HORJY** to verify the particle size distribution of deposited particles. Various analysis modes, including topography and Kelvin modes, can be applied to determine the particle size and some electronic properties of the sample. For the second sampling campaign, additional electron microscopy was performed at **BOSCH** and **ULL** to further investigate the particle size distribution and composition.

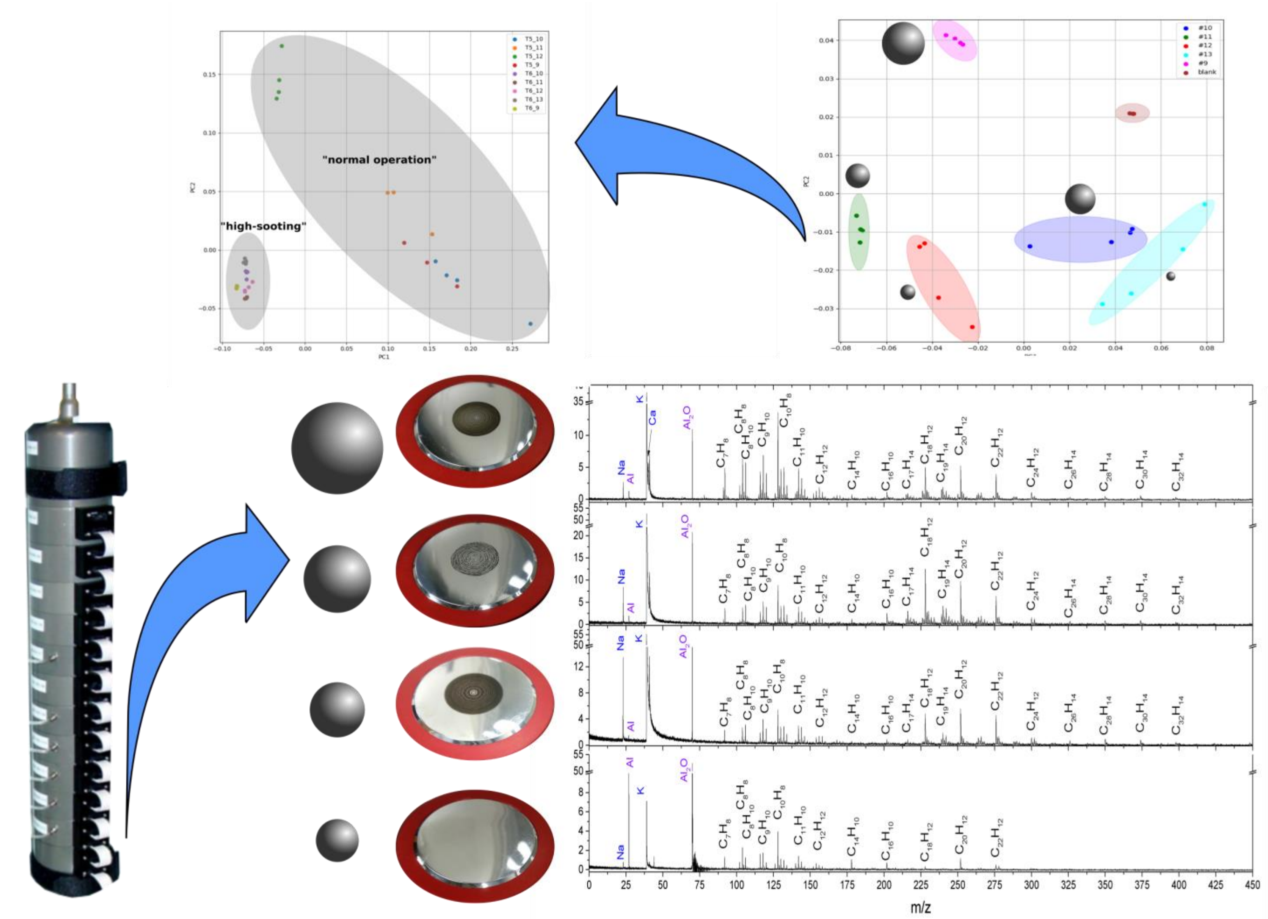

Figure 0-1 Overview of particle discrimination by chemical analysis of deposited size-selected samples. Particles are size-selected during collection with the nanoMOUDI II impactor (TSI), analysed using mass spectrometric techniques (ULL), and finally principal component analysis is applied in order to discriminate and identify particle sources.

The results of the sampling campaign are extensive. Two key aims were to discriminate particles by their size and by their surface chemistry (and thus source) for different engine working points. Discrimination by size was achieved through the use of both size-selective collection instruments (Nano-DMA and nanoMOUDI) and atomic resolution analytical methods (AFM and TEM). This size discrimination was highly effective, allowing the collection and measurement of particles down to 10 nm. The discrimination of both particle type and particle source by size was possible upon adoption of this new measurement strategy.

Discrimination by surface chemistry was achieved through the use of appropriate and powerful analytical techniques, including the mass spectrometric techniques L2MS and SIMS. The particle collection and analysis methodology is summarised in Figure 0-1. The application of principal component analysis to mass spectrometric data allowed the definitive discrimination of particles from different sources, as well as the identification of those sources, even for samples where all particle sizes were collected simultaneously (i.e. non size-selected samples). Where size-selection was applied during particle collection, particle characterisation allowed a detailed description of the size-dependent chemical composition of particulate matter, including attribution of particle sources (combustion versus secondary particle sources) and a direct link to fuel and lubricant raw composition or combustion products.

Finally, the results of this deliverable are put into the context of the ongoing progress in **WP3** towards better understanding the particulate matter in the generic single cylinder test motor. The first LII measurement campaign is scheduled to take place at **BOSCH** in **M18**. The expected results of the first LII measurements campaign on the generic test engine are the optimisation of the experimental set-up, and the relative evolution of soot volume fractions at one (or more) engine operating point. Future applications of the LII analysis will include measuring more, and diverse, operating regimes and determining the impact of the catalytic stripper at various locations in the exhaust line. One particularly interesting possibility of the LII measurement campaign is in comparing LII results to future collected particle measurements (i.e. linking in-situ particle size characterisation with ex-situ size-selective chemical characterisation). The composition data presented in this document will serve as calibration targets for the detailed models developed as part of the model guided application. One component of this is to predict the boundary conditions, or range of expected characteristics, in terms of **particle morphology**, **composition**, and **size** at the origin and at the tailpipe and provide these as a guide in the form of quantitative estimates and qualitative trends (as a function of operating conditions) to the measurement devices.

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Project partners:

#	Type	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.
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