



Portable Nano-Particle Emission Measurement System

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Publishable Executive Summary

This report concerns the current progress in the PEMs4Nano project towards characterization of particles emitted by a generic single-cylinder test engine in the exhaust line. Sampling of solid particulate matter was performed using various instruments, to obtain a detailed and complete particle characterization with a wide variety of offline analytical techniques. The obtained size-dependent chemical composition of particulate matter serves as an input for the modeling activities meant to describe the particle formation and evolution from engine to tailpipe.

One of the objectives of Work Package 3 “Measurement integration into system development” is to provide insight into particle dynamics in single-cylinder engine systems, in particular, the evolution of particle characteristics through the exhaust after-treatment configurations. A combination of various analytical techniques was used to achieve this goal – from in-situ monitoring of the particle properties (size distribution, mass, mobility, and aerodynamic characteristics) to the analysis of the chemical composition of particulate samples collected on various substrates.

In particular, this report focuses on Task 3.1 “Particle characterization and evolution on single-cylinder engine”. We 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 substrates. Previous particle sampling campaigns, described in detail in Deliverables D2.3 and D3.1, were focused on the characterization of size-selected particulate matter sampled from the exhaust port of the engine. In the last particle sampling campaign, described in this report, the aim was to study the impact of after-treatment systems, such as catalytic strippers, on particle characteristics. To assess the efficiency of an after-treatment system, particles before and after the system have been collected and analyzed with mass spectrometric techniques, microscopy (scanning and 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 ionization 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 volatilization and ionization of surface molecules, which are separated 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 modeling particle growth mechanisms). Atomic force microscopy (AFM) and Tip Enhanced Raman spectroscopy (TERS) are performed at **HORJY** to verify the particle size distribution and chemical identification of deposited particles. Various analysis modes, including topography, can be applied to determine the particle size. For the fourth sampling campaign, additional electron microscopy was performed at **BOSCH** and **ULL** to further investigate the particle size distribution and composition.

The results of the sampling campaign are extensive. Size-selected particulate matter was studied. 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 impact of a catalytic stripper (used in particle measurement instruments and vehicle after-treatment system) on particle characteristics was also evaluated. Particulate matter was discriminated by surface chemistry through the use of appropriate and powerful analytical techniques, including the mass spectrometric techniques L2MS and SIMS. The application of principal component analysis to mass spectrometric data allowed the definitive discrimination of particles collected before and after the after-treatment system, achieved even for samples where all particle sizes were collected simultaneously (i.e. polydisperse samples) and the gas phase. When size-selection was applied during particle collection, particle



characterization allowed a detailed description of the size-dependent chemical composition of particulate matter which enabled the evaluation of the size-dependent efficiency of after-treatment systems.

Finally, the results of this deliverable are put into the context of the progress in WP3 towards better understanding the particulate matter and its evolution in the generic single cylinder test engine. 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 De Lille
7	IND	IDIADA	Idiada Automotive Technologie SA
8	IND	HORJY	Horiba Jobin Yvon S.A.S.
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