Measurement and Characterisation of ultrafine particles in engine exhausts

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Abstract / Kurzfassung:

On-road motor vehicles are important sources of ultra-fine particulate matter (PM) emissions, which present acknowledged health and environmental risks. There is currently a critical lack of certified measurement procedures for the smallest particles (below 23 nm) under real driving conditions. The H2020 PEMS4Nano project (www.pems4nano.eu) aims to develop a portable emission measurement system for particles below 23 nm, providing a contribution to future regulations on emissions in real driving conditions. The development of this instrument (and the associated measurement methodology) requires a deep understanding of the emitted particle characteristics, including a thorough characterization of the size-dependent chemical composition, structure and morphology.

Key Words / Schlagworte:
Chemical Composition; Model Guided Application; PEMS; Real Driving Emissions;

1 Introduction / Einleitung

With ever-increasing traffic, citizens may be exposed to particle emissions that are invisible to the naked eye. These particles can be as small as 10 nanometers and are found in urban areas with dense traffic. In the GV2-2016 call, the EC therefore called for the development of measurement procedures of particles down to 10nm, in particular, in real driving conditions (real driving emissions, RDE).

Main objective of the project is the development of robust and reliable measurement equipment for particles down to 10 nm supporting research and legislation; the fundamental understanding of formation, composition, size distribution and transport of exhaust particles in order to support the development of the measurement equipment including the impact on the measurement procedure; and finally, to identify robust and reliable measurement procedures for particles down to 10 nm verified under real driving conditions. The technology development comprised a laboratory-based equipment for research/certification and PN PEMS for RDE, the optimization of Condensation Particle Counter (CPC) with D_50 ≤ 10 nm and the optimization of PEMS Catalytic Stripper (CS) to at least 50 % detection efficiency at 10 nm. Regarding the understanding of the particle formation process, a Model Guided Application (MGA) was developed combining physico-chemical and statistical algorithms to simulate the particulate emissions in IC engine driven vehicles. This allows to understand the sensitivity of PM, PN PN, the particle size distribution, the aggregate composition and morphology as a function of fuel characteristics, the engine operating modes, after-treatment and RDE attributes as well as the thermodynamic boundary conditions at various sampling points. The instrumentation developed was validated with measurements on engine and roller test benches as well as real driving emission tests.

2 Measurement System

The goals in PEMs4Nano are to develop the following:

- Two measurement systems: Devices for stationary and
  mobile applications will be made suitable for the reliable measurement of 10 nm particles. To achieve this, the particle losses of the systems need to be minimized, the losses as function of particle size have been characterized, and the measurement devices need to be stable over time. To avoid measurement artefacts and to provide reliable measurements of solid particles, the systems must include a catalytic stripper to remove volatiles.
- Robust procedures: Measurement conditions (i.e. measurement procedures) will be determined for which the losses, detection limits and tolerances are acceptable for reliably detecting solid 10 nm particles.

- Model-guided application: A simulation workflow is developed to calculate the particle emissions. The model describes the full particle trajectory from inside the engine to the tailpipe end and is essential to make the future EU certification tests as robust and reliable as possible.

2.1 Step 1: Optimization and calibration of the CPC for PEMS use

A 23 nm CPC (TSI PEMS-CPC as used in HORIBA OBS-ONE PN series) was used as the base for optimization. By adjusting the temperatures of the saturator and condenser of the instrument, it is possible to reach the initial set target for particle detection efficiency for thermally conditioned CAST flame soot of greater than 50% at 10nm.

2.2 Step 2: Optimization and calibration of solid particle counting system

This includes particle count reduction factor (PCRF) evaluation and system efficiency measurement for PEMS use. One of the major improvements within the system is the optimization and development of the CS as it was determined to be the element with the highest considered particle losses in sub-23nm regime. The general purpose of this component is to remove volatiles and semi-volatiles, so that the PEMS will only detect the solid particles. Being part of the volatile particle remover (VPR) it is located between the first dilution and the second dilution stage. It is important to verify, that the new system reliably counts only the solid particles as there is a trade-off in particle penetration rate and sufficient removal of volatiles (e.g. hydrocarbons).

3 Size-dependent chemical composition

The development of a reliable measurement procedure requires a prior thorough understanding of the emitted particle characteristics (morphology, structure, chemical composition, volatility, reactivity), and their dependence on size. To support the investigation of the chemical composition of size-selected particles, particulate matter emitted by a gasoline direct injection engine has been collected and analysed.

- Particulate matter probed in this study was produced with a generic single-cylinder engine (Bosch) which can be operated in various working regimes. Five size bins ranging from 180 to 10 nm were analysed.
- The chemical characterisation of the collected particles is performed using an in-house two-step laser mass spectrometer (L2MS, Faccinetto et al., 2015). Combining gentle (low-fluence) laser desorption and various ionization wavelengths. Additional high-resolution chemical mapping is performed using a commercial Secondary Ion Mass Spectrometer (IONTOF).

- The very rich mass spectra of size-selected particles require powerful statistical treatment to unveil subtle differences in the chemical composition. This is done through principal component analysis (PCA) and hierarchical clustering analysis (HCA). Chemical species responsible for these variations can thus be undoubtedly identified and the size-selected particles can be discriminated and classified according to their origin. Moreover, the influence of various experimental parameters (engine regime, fuel additives, lubricating oil, mechanical wear etc.) can be easily identified.

The combination of mass spectrometric studies with statistical procedures provides evidence of the chemical composition size-dependence. This information represents critical physico-chemical data in the development of a reliable portable device for the measurement of ultra-fine particles emitted from automotive engines.

4 Model-guided application (MGA)

Physics-based models and statistical methods have been developed to support the measurement procedures by providing:

- Insight into the physical processes responsible for particle emissions, starting from the formation of particles in the engine, the evolution of particle emissions in the exhaust system, through to sampling of the particles in the measurement system.
- A method to relate the chemical composition of the particles to how they were formed in the vehicle.
- An assessment of the sensitivity of the particle size distribution and particle number emissions to the engine operating (e.g., load, speed, etc.) and sampling (dilution, temperature, etc.) conditions.
- A method to estimate quantities that may be difficult to obtain experi mentally, for example, in-cylinder temperature, fuel distribution, etc.

4.1 Fuel Model

The MGA uses a surrogate fuel model to describe the chemical reactions that govern the combustion of the fuel and the formation of emissions, including NOx, CO, unburned hydrocarbons, and the gas-phase chemical species (precursors) that lead to the formation of particles.

4.2 In-cylinder combustion model

A stochastic reactor model (SRM) is used to simulate the in-cylinder combustion process. The SRM uses physico-chemical models to describe the effect of inhomogeneities (for example, temperature stratification due to uneven combustion or heat transfer in the cylinder, or inefficient mixing of the fuel due to aspects of the injection process) on the formation of emissions within the engine. The SRM includes a population balance model based on the techniques described by Kraft (2005) to describe the formation of particulate emissions in the engine.

4.3 Exhaust after treatment models

A set of models that combine heat transfer, reactive flow, surface chemistry and the same population balance model as used in the in-cylinder combustion model have been developed to simulate the evolution of the particles generated in the engine as they pass through the after treatment devices in the tailpipe of a vehicle.

4.4 Understanding what happens to the particles in the measurement devices

Given knowledge of the size distribution of the particles and experimental characterisation of transfer functions for the components in the measurement system, the size-dependent particle losses between the tailpipe and the detector in the measurement device can be quantified. This is critical to ensuring a robust measurement system that can detect the smallest particles and that can relate the number and size of the particles at the tailpipe of the vehicle to the number of particles seen by the detector.

4.5 Chemical composition and morphology

Data has been collected throughout the project to provide input to support the development and testing of the models. In particular, the particle size distribution, chemical composition and morphology of the particles in the engine (as opposed to tailpipe) exhaust has been characterized.

5 Summary and Outlook / Zusammenfassung und Ausblick

Two reliable and robust measurement systems (for stationary and mobile applications) and measurement conditions (i.e. measurement procedures), for which the losses, detection limits and tolerances are acceptable for detecting 10 nm particles, have been developed for RDE certification. The measurement devices and procedures have been developed in parallel with Model Guided Application (MGA) workflow to understand what happens to the particles, from their formation in the engine, through the tailpipe and into the measurement system.

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