Chemical characterisation of the particulate matter emitted by automobile motors: the PEMs4Nano project

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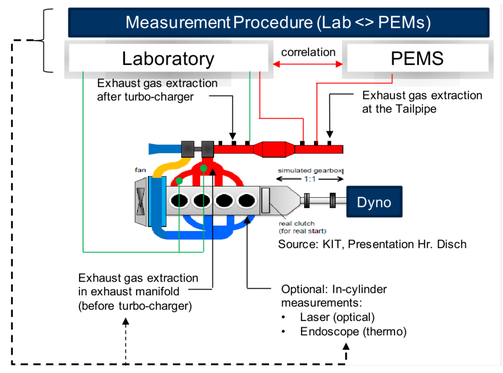
Scientific motivation

Particulate emission from vehicles is fast becoming a prominent societal concern due to the toxicity of particles released from motors. There is a critical lack of certification procedures under real driving conditions and for ultrafine particles (the smallest particles down to 10 nm). The development of such measurement procedures would provide an important contribution towards both the future regulation of particle emissions and the development of new engine technologies. In the framework of the PEMs4Nano project (H2020), particle characteristics, including their size-dependent chemical composition, will be investigated at various locations in the tailpipe. The overall objective of the PEMs4Nano project is to develop/achieve measurement procedures down to 10 nm, providing a contribution to future regulation on particle emissions, in particular in real driving conditions.

PEMs4Nano concept

The PEMs4Nano project (P4N) addresses the development (based on current direct injection gasoline engines) of measurement procedures down to 10 nm, providing a contribution to future regulation on particle emissions, in particular under real driving conditions, via a collaborative research approach.



Portable Emission Measurement System

- ***Laboratory single cylinder test engine***
- ***In-situ measurement of gas phase***
- ***Tailpipe and engine sampling of particulate matter***
- ***Ex-situ physicochemical characterisation***
- ***Particle growth and transport model***
- ***Real driving conditions on test track***

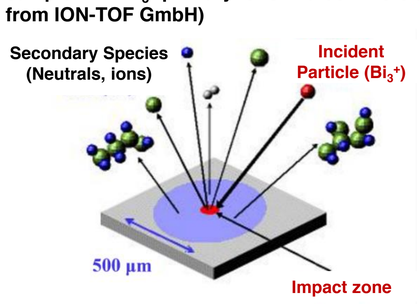
Consortium

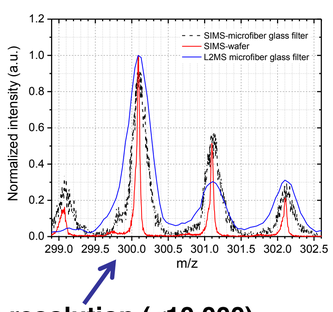
The global aim of the project is to develop a portable measuring device capable of the *in-situ* quantification of particulate matter at sizes down to *at least* 10 nm in gasoline motor exhaust. The PEMs4Nano project is being tackled by an international consortium of industrial and academic partners, coordinated by HORIBA Europe GmbH. Project partners include Robert Bosch GmbH, Computational Modelling Cambridge Ltd, TSI GmbH, the University of Cambridge, Université des Sciences et Technologies de Lille, IDIADA Automotive Technology SA, HORIBA Jobin Yvon SAS, and Uniresearch B.V.

The role of the PhLAM laboratory partner at Uni. Lille will be to participate in the chemical characterisation of particulate matter down to 10 nm using the four main techniques outlined below (Time of Flight Secondary Ion Mass Spectrometry, Desorption/ionisation Mass Spectrometry, Infrared Spectroscopy and Raman Spectroscopy)

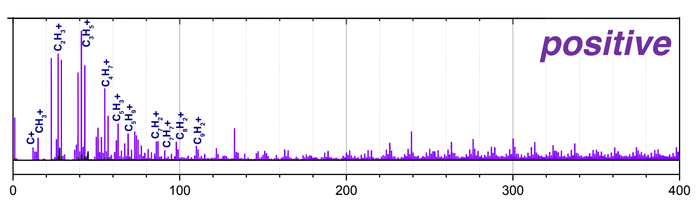
Secondary ion mass spectrometry

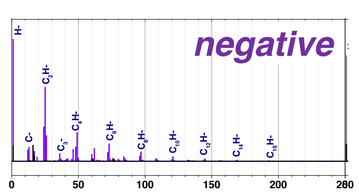
Ions generated in positive or negative polarity mode by bombardment of soot sample with Bi_3^+ primary ions in a commercial apparatus (TOF.SIMS^5 instrument from ION-TOF GmbH)





High spatial resolution and mass resolution (<10,000)

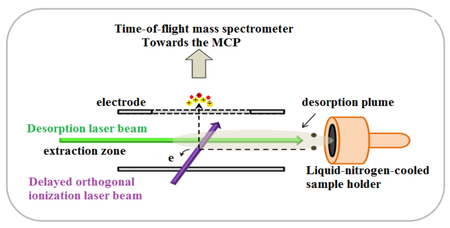




Representative SIMS spectra of soot samples (+/- modes)

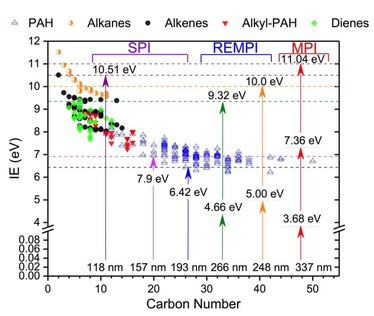
- **Identification of organic carbon (aliphatics, aromatics, *etc* in positive mode) and elemental carbon (C_n in negative mode)**
- **Additional components: metals, oils, sulfur-containing species**
- **Surface mapping capability**

Desorption/ionisation mass spectrometry

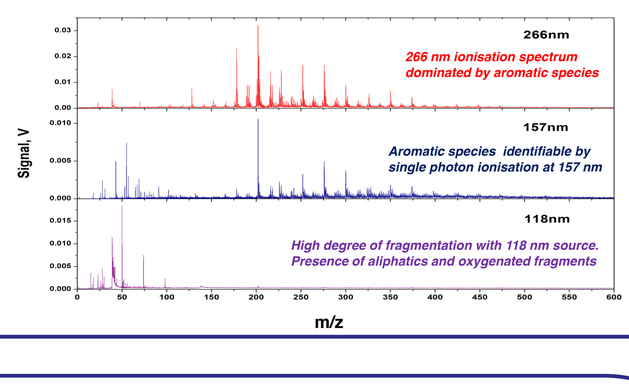


A novel two laser mass spectrometry technique developed at Uni. Lille to study deposited soot samples, where the first laser (532 nm, ~400 µJpulse^{-1}) desorbs material from a sample, resulting in an expanding plume which is orthogonally ionised by a second laser (266, 157, or 118 nm) for measurement by ToF-MS.

Ionisation schemes of molecular species as a function of wavelength

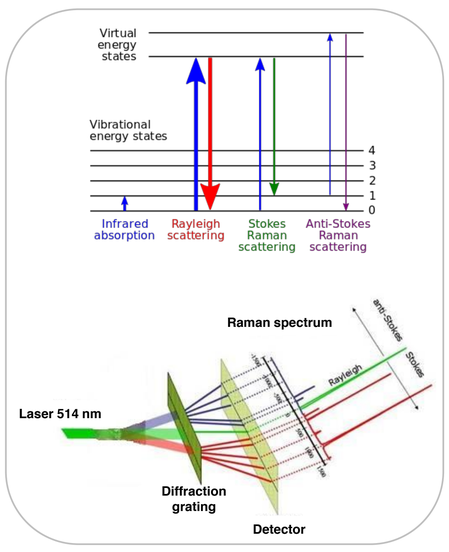


- **Three ionisation sources giving access to REMPI and SPI regimes (allows distinction between aliphatic & aromatic compounds)**
- **Mass resolution ~1000, m/z < 800**
- **High sensitivity to PAHs: DL ~ 0.1 fmol per laser shot**
- **Semi-quantitative analysis of carbon content of soot samples**



Representative L2MS spectra of soot samples at three different ionisation wavelengths

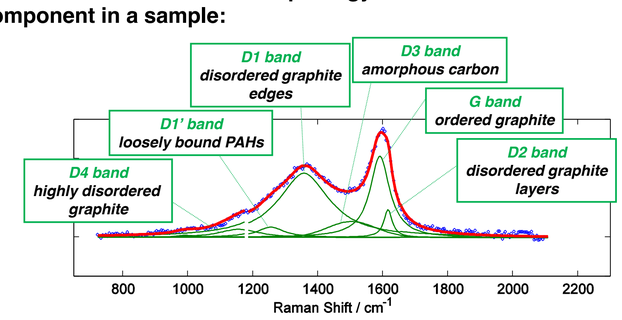
Vibrational spectroscopy



Fourier Transform Infrared micro spectroscopy can be performed in the mid infrared in reflectance or transmission mode using a commercial Bruker Vertex 70 FTIR spectrometer coupled to an optical microscope (Bruker Hyperion). Characteristic absorption bands in the measured spectra allow the identification of chemical functional groups.

Raman spectra (inelastic scattering of a filtered 514 nm laser) can be measured using a commercial Invia reflex spectrometer (Renishaw) coupled with an Olympus microscope (BXFM).

Deconvolution of the characteristic Raman band of soot particles can aid in the identification of the morphology and structure of the carbon component in a sample:



Ambitious Targets

- **To reliably and reproducibly measure the ultrafine particle component of gasoline engine emissions under real driving conditions**
- **To this end, the PhLAM laboratory partner will provide:**
  - **Characterisation of volatile and non-volatile particles emitted from a GDI engine in terms of surface and bulk chemical composition, structure and morphology via mass spectrometry and vibrational spectroscopy measurements (for integration into a particle growth and transport model)**
  - **Differentiation (as a function of size) of particles as a function of their origin in the exhaust system. The following groups of particles will be distinguished in the collected samples: *elemental carbon* (by targeting C_n^- ions in ToF-SIMS); *organic carbon* (by targeting aromatics and oxygenated species); *metals*; *oils*; and *sulfur compounds* (by targeting HSO_4^-, SO_3^- ions).**
  - **Determination of the efficiency of a catalytic stripper in reducing the number of semi-volatile species released from the exhaust system**

Further information

For further information regarding the PEMs4Nano project, or to subscribe to the newsletter, visit the project website at:

http://www.pems4nano.eu/

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