Measuring ultrafine particles emitted by gasoline direct injection engines: the PEMS4Nano Project

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Portable Nano-Particle Emission Measurement System

H2020 Green Vehicles action

What's the challenge?

The challenge is to develop detectors and robust procedures, in order to reliably measure the particle number concentration (PNC) down to 10 nm in the exhaust gas.

PEMs 4Nano

Engine

Combustion engines provide the power to move the vehicle by burning fuel in the cylinders.

Exhaust

Emissions resulting from the combustion contain CO, CO_2, water, unburnt hydrocarbons, particles and NO_x.

Aftertreatment

After-treatment systems are used to reduce emissions. They include, among others, three-way catalysts and particle filters.

Detection

Currently, exhaust particle measurements are designed to detect the number of particles larger than 23 nm.

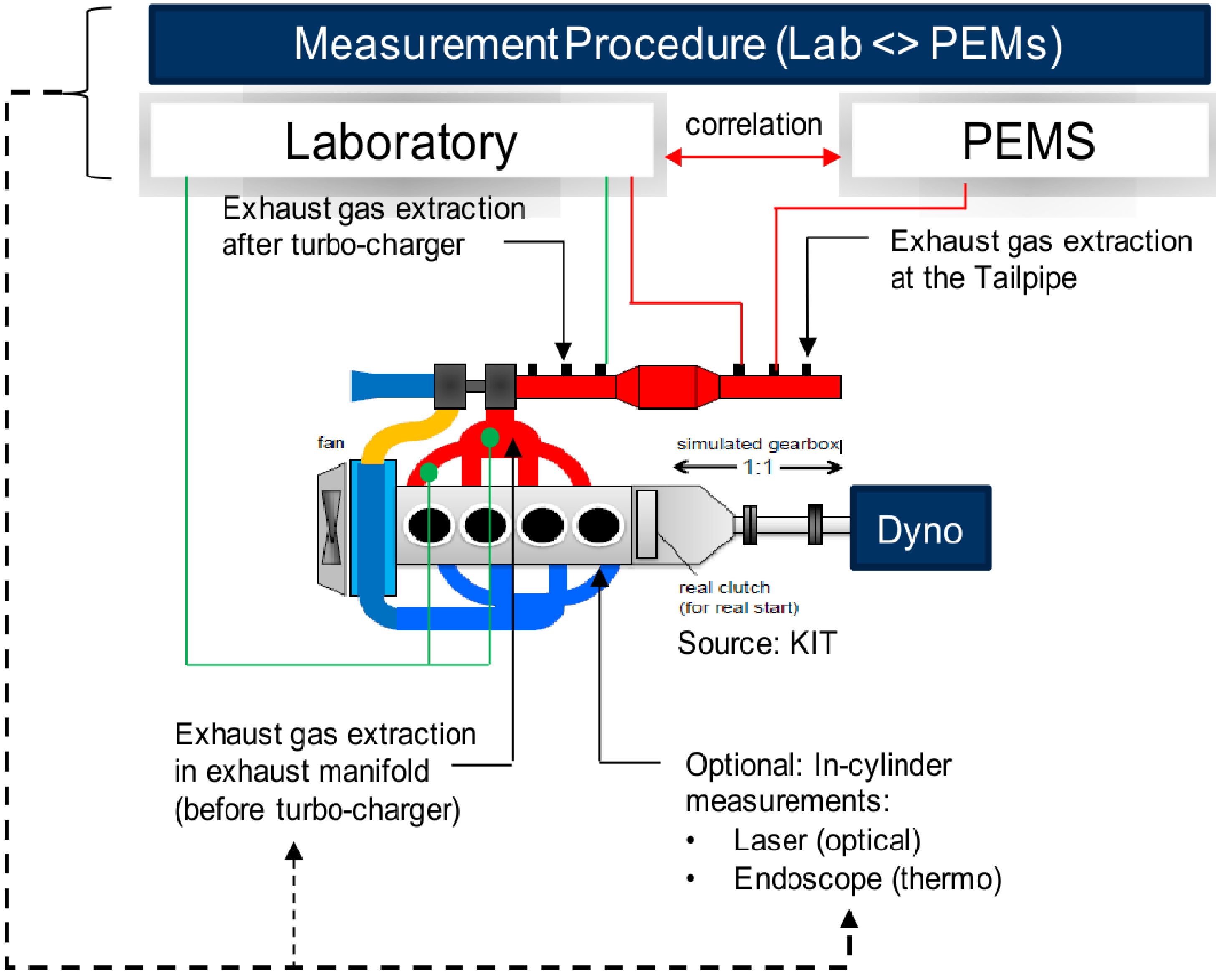
The partners in PEMs4Nano will develop a portable device and a robust procedure to detect particles down to sizes as small as 10 nm.

Particles form in the engine ... ... travel down the exhaust line ... ... and are detected at the tailpipe.

- Current certification procedures are not able to detect **ultra fine particles** (< 23 nm)
- PEMs4Nano will develop **robust and reliable measurement** procedures for both the development of **lower emission engine** technologies, as well as serving as a solid basis for **new regulations**

Portable Nano-Particle Emission Measurement System

- **Development of Condensation Particle Counter** and catalytic stripper



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

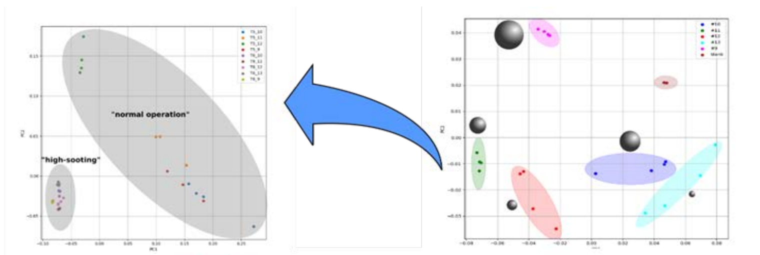
Physico-chemical characterization of the smallest particles emitted by internal combustion engines

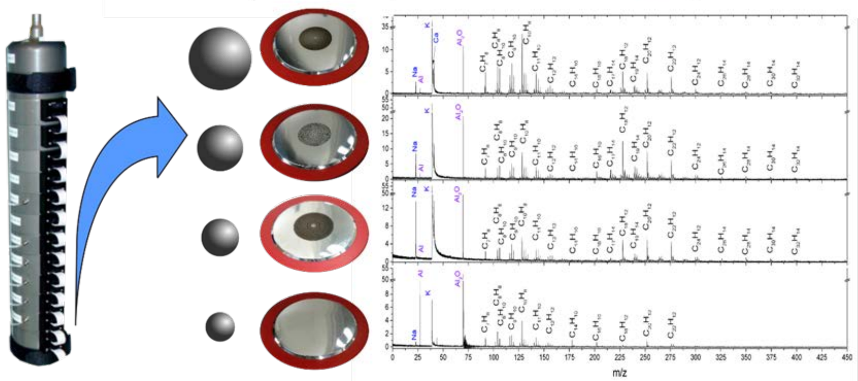
PEMs 4Nano

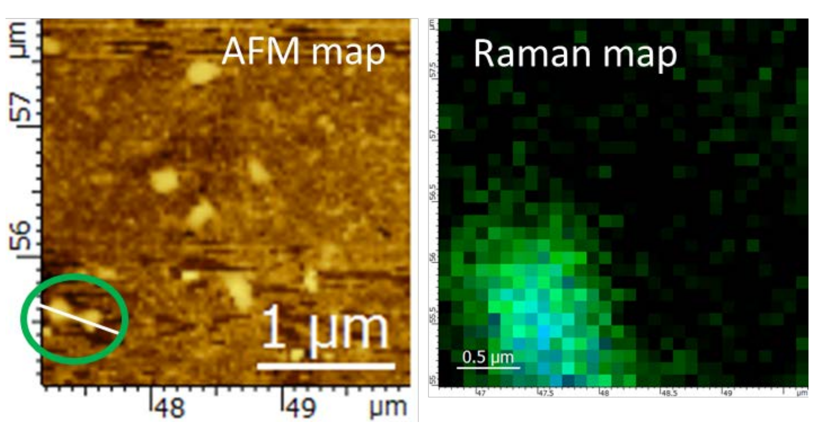
Size-selective sampling and off-line analyses

by mass spectrometry, electron and atomic force microscopy, Raman spectroscopy

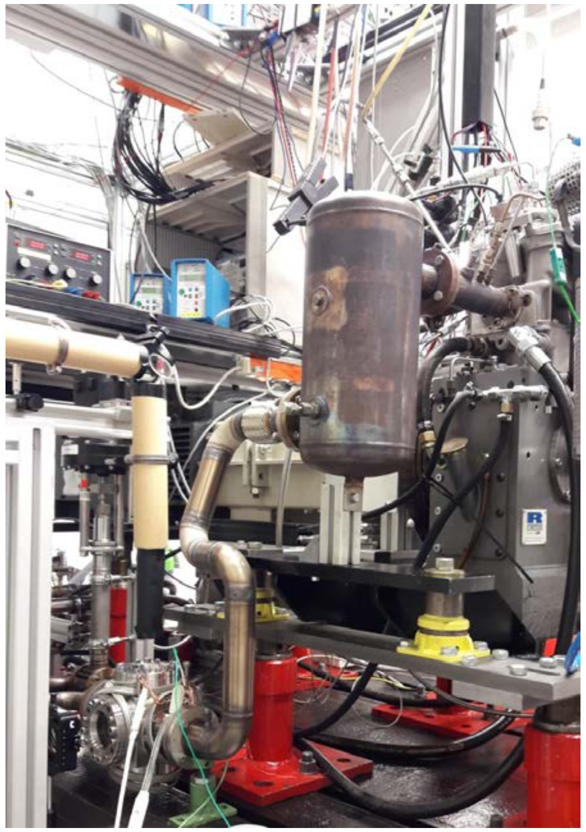
+ advanced statistical anlysis

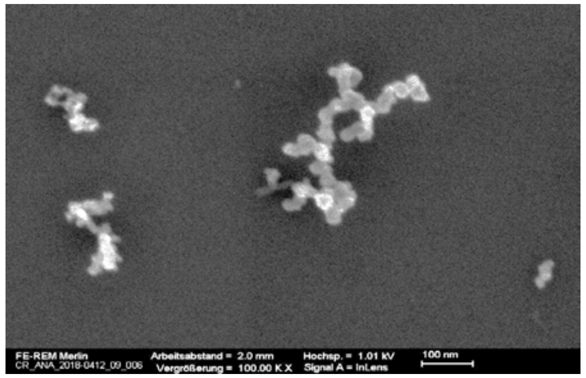




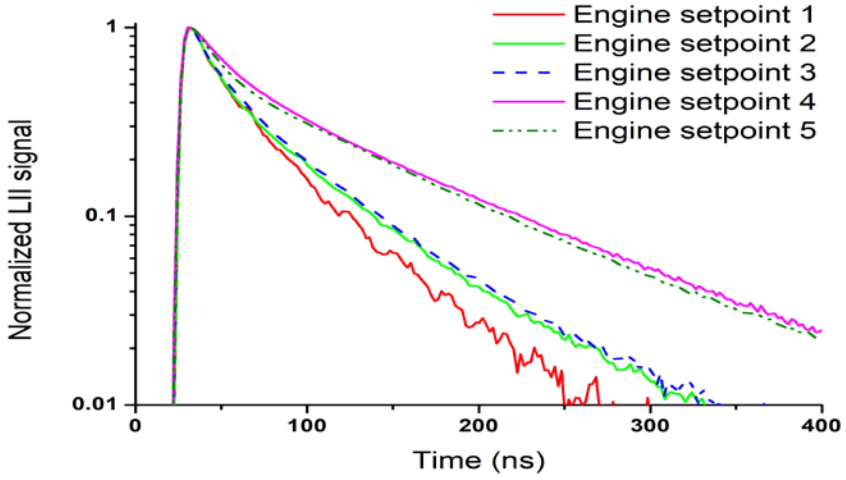


Single Cylinder Engine @ Bosch, Renningen





On-line analysis by Laser-Induced Incandescence



Results & importance

Extensive database on size-dependent particle structure, morphology, chemical composition … for various working regimes of the single cylinder engine – used as particle generator

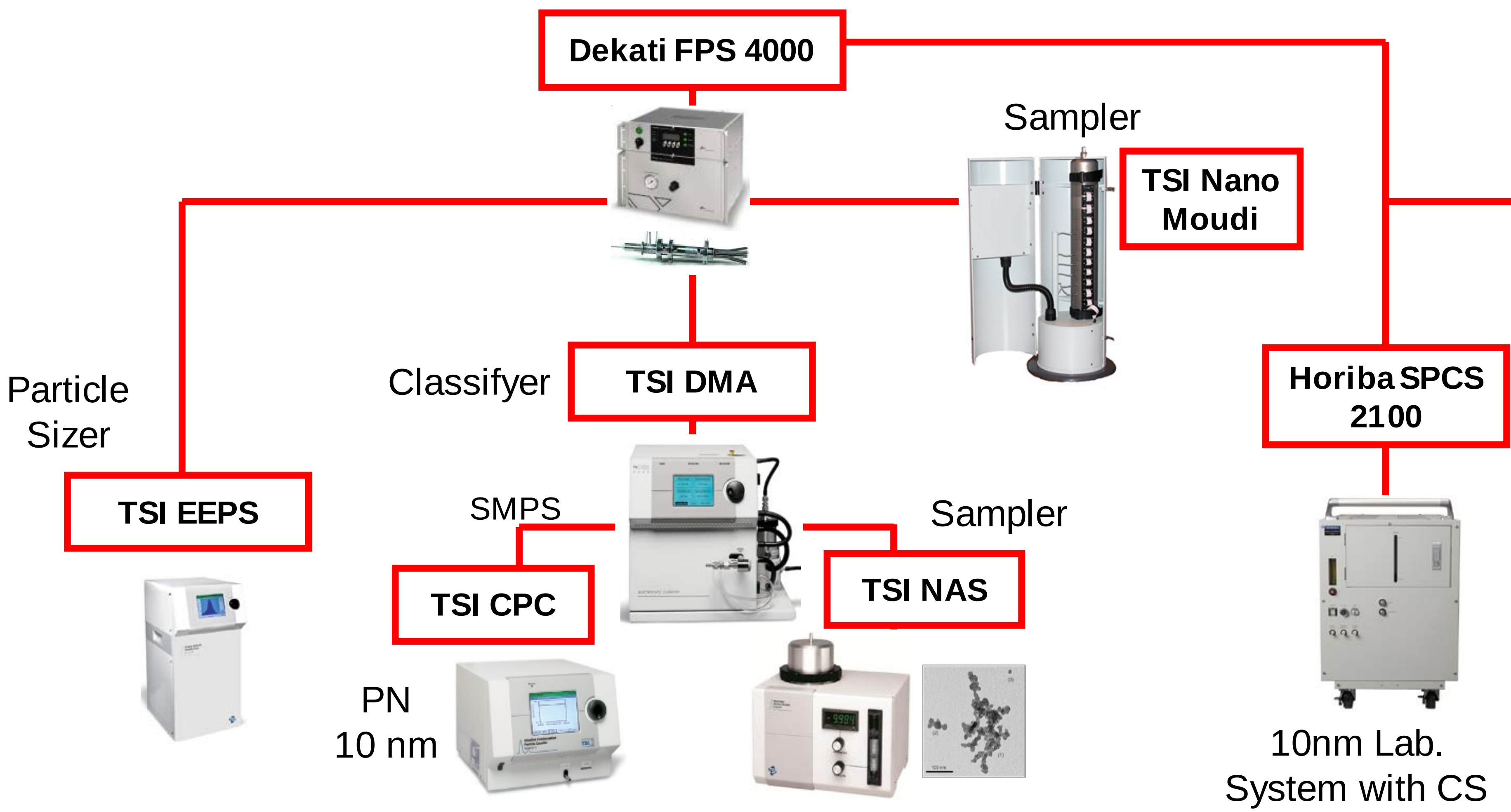
Input for the complex model developed by CMCL & U. Cambridge

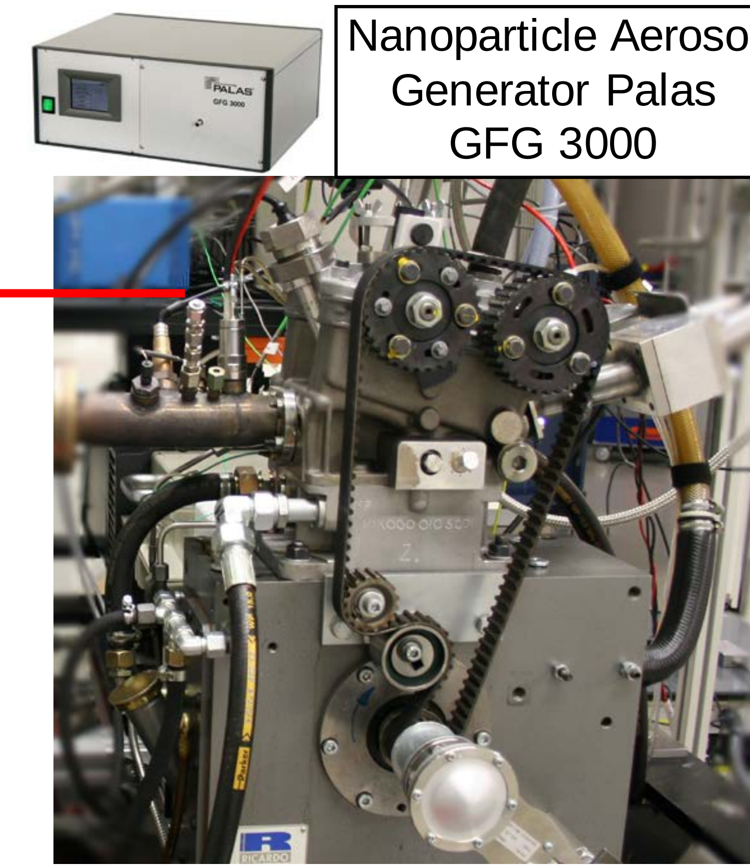
PEMS4Nano prototype optimization & Possible use in other projects for engine optimization

… Future implementation on Multi-Cylinder Engine

Université de Lille UNIVERSITY OF CAMBRIDGE BOSCH Invented for life HORIBA Scientific TSI Applus IDIADA cmcl innovations

Experimental setup – Single Cylinder Engine





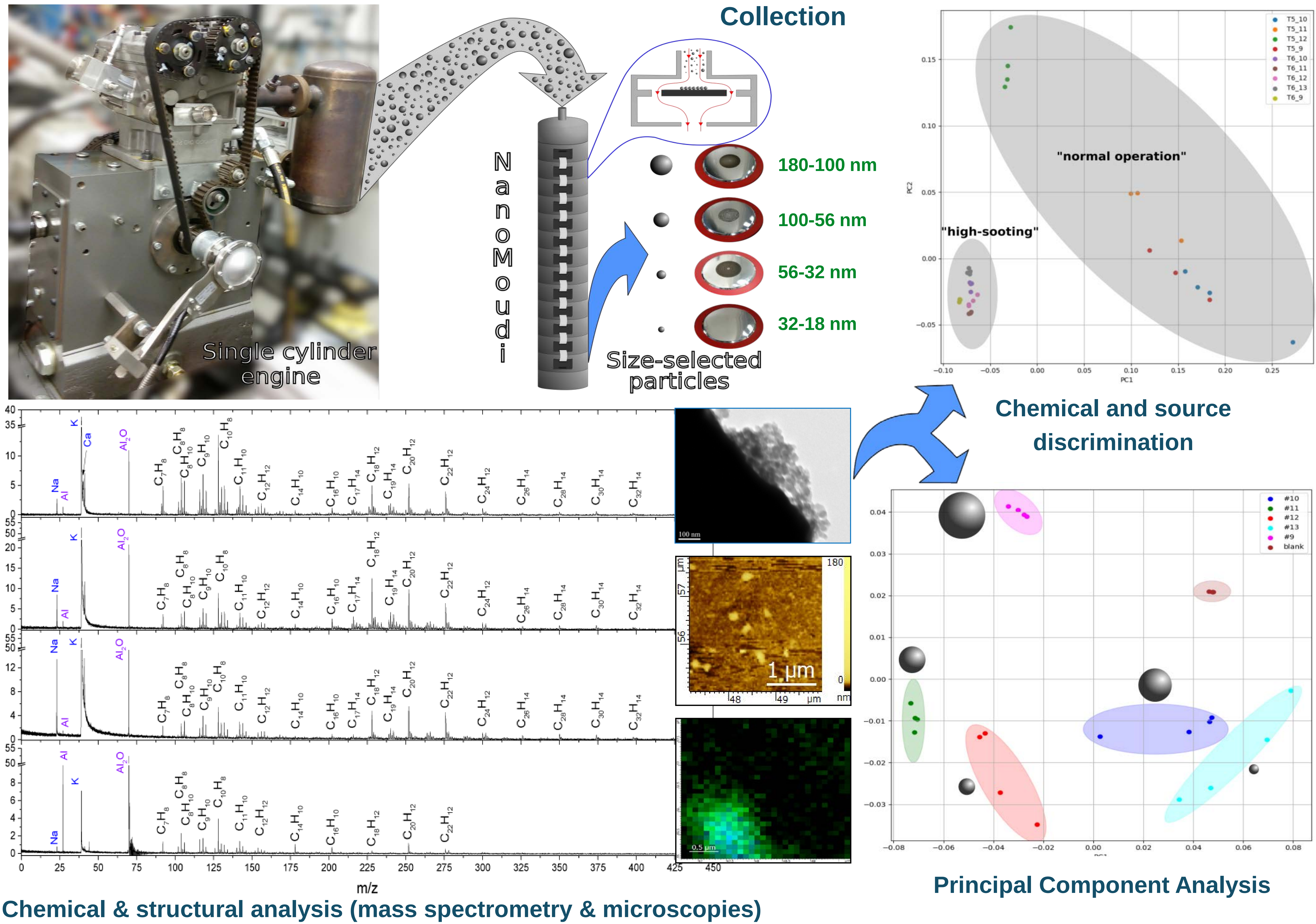
- Single cylinder engine
- Displacement: 449 cm³, ε=12.5
- GDI and PFI mode possible

ıine Exhaust Particle Sizer
Particle Sampler

PFI = Port Fuel Injection
GDI = Gasoline Direct Injection

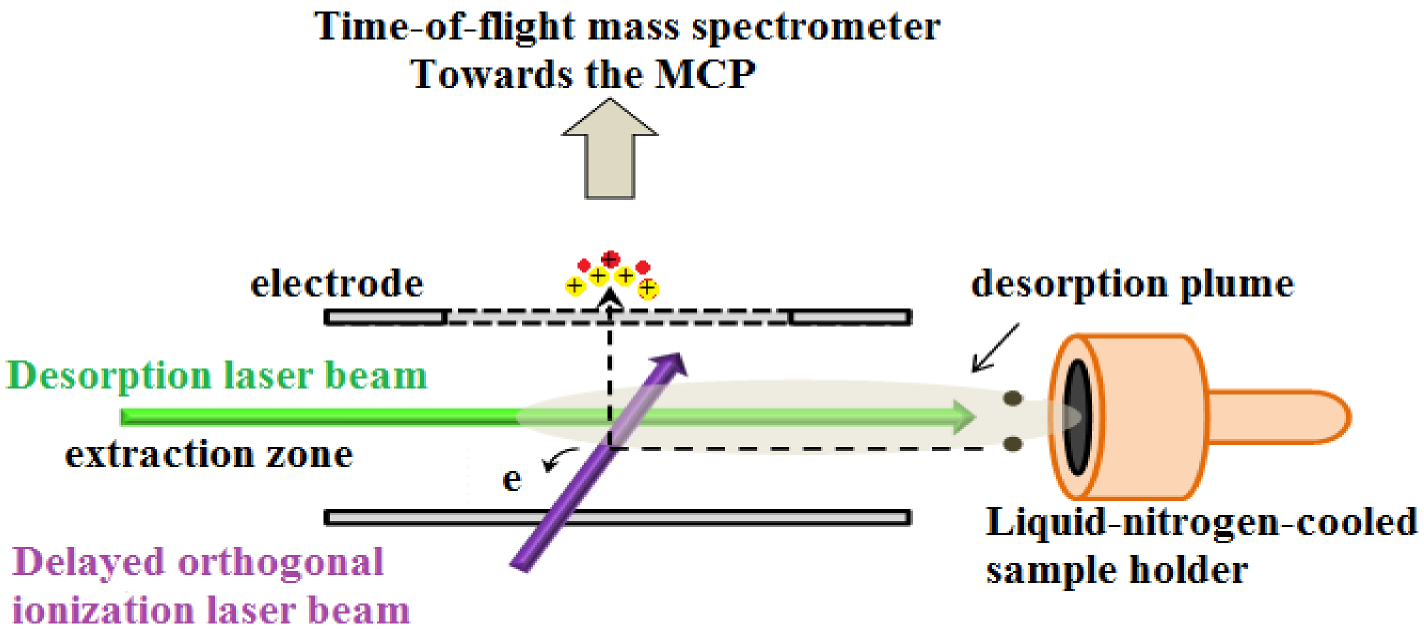
DMA = Differential Mobility Analyzer
SMPS = Scanning Mobility Particle Sizer

Chemical composition analysis



Mass spectrometry techniques

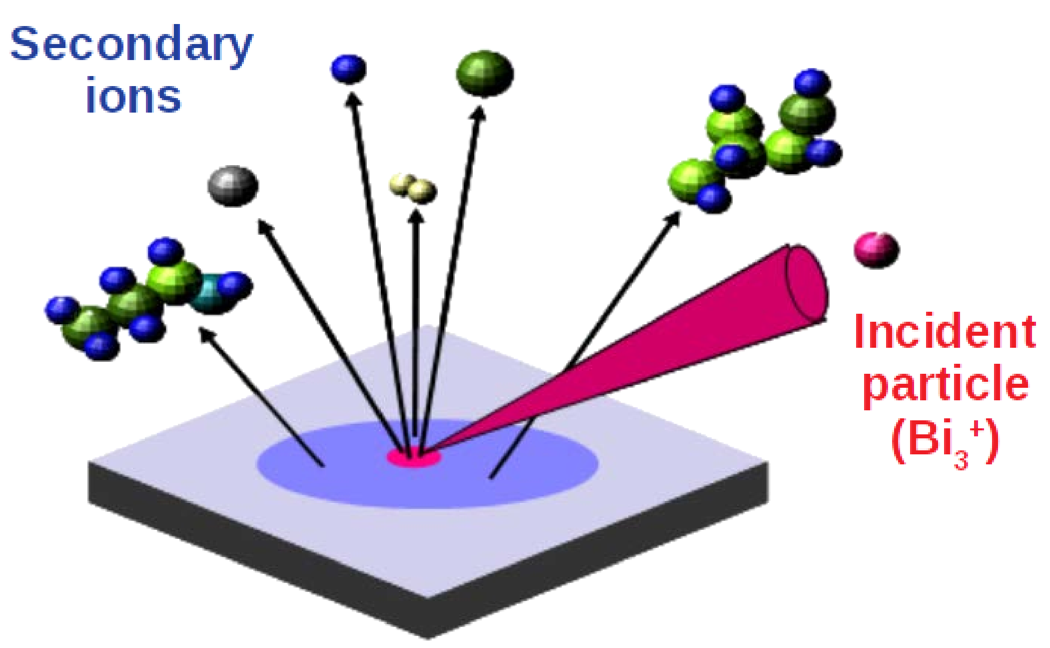
Two step Laser Mass Spectrometry (L2MS)



- Controlled fragmentation
- Ultra-sensitive to PAHs (attomol)
- Selective (laser ionisation)

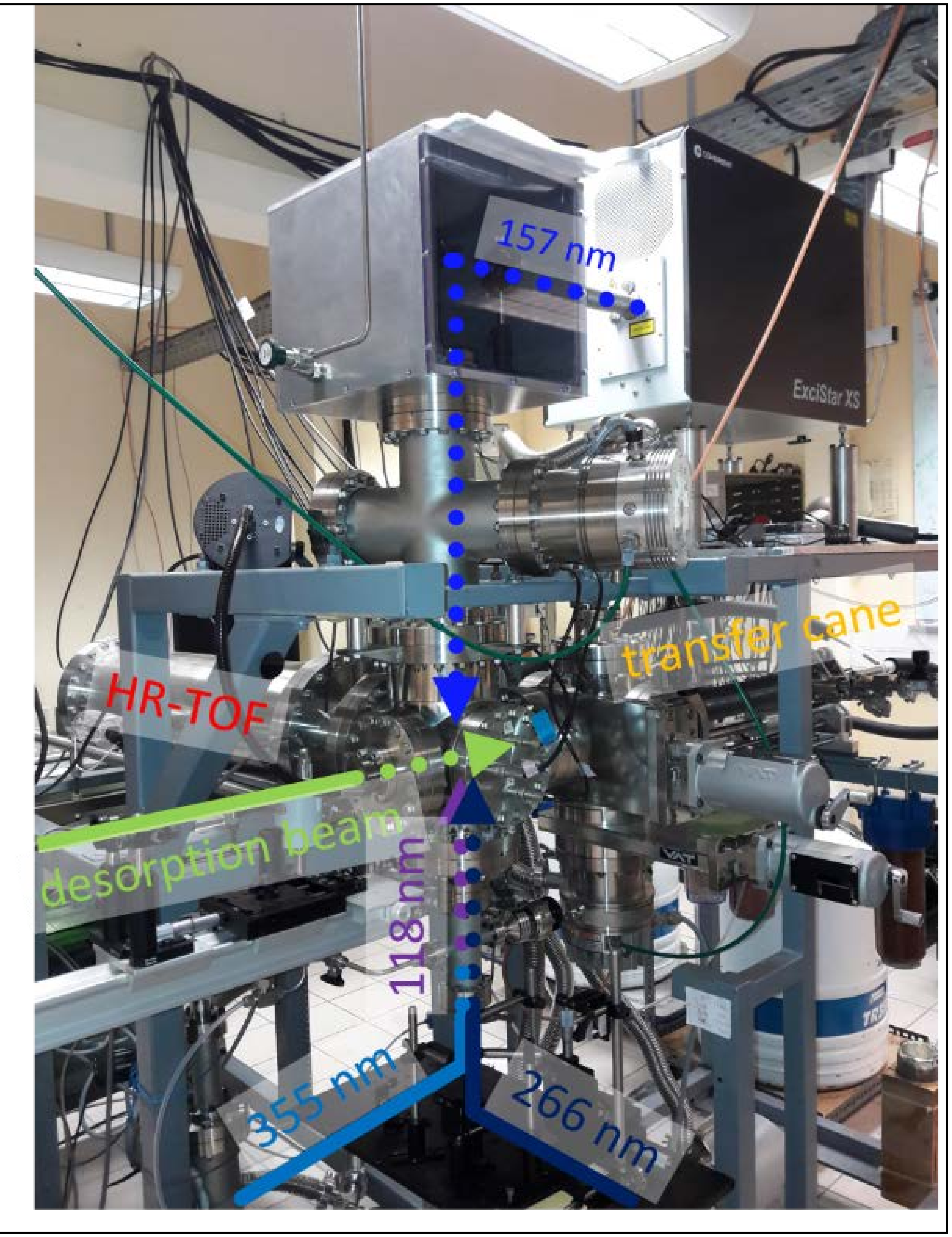
New High Resolution Laser Desorption Ionisation Mass Spectrometer (HR-L2MS)

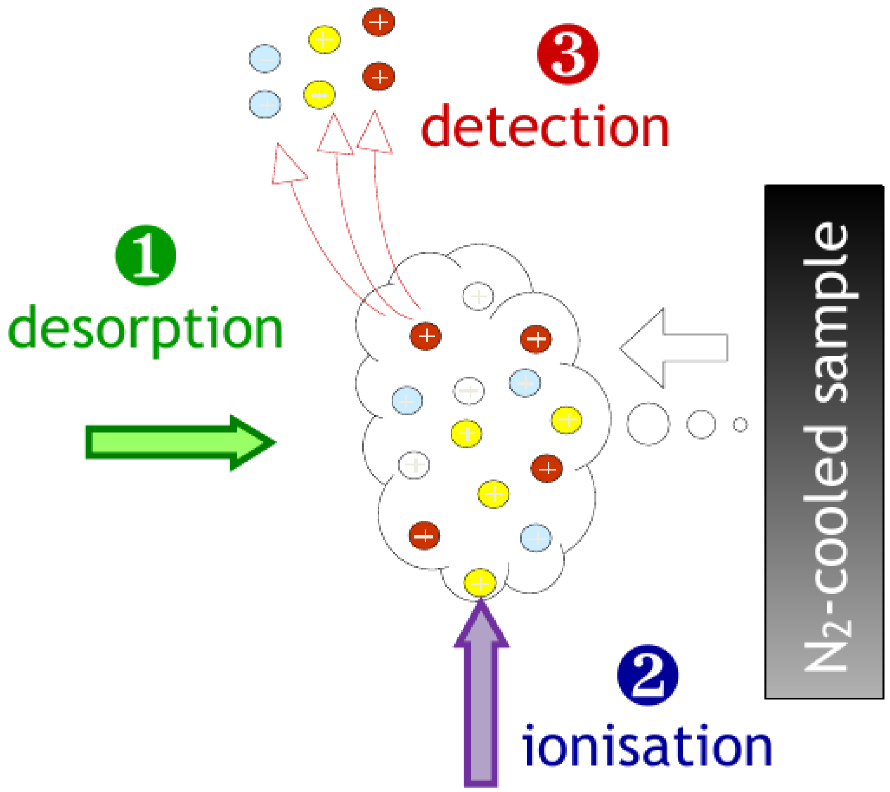
Secondary Ion Mass Spectrometry (ToF-SIMS)



- High fragmentation
- High mass resolution
- Mapping, depth profiling

Ionisation sources for L2MS chemical characterisation





1 ***LASER DESORPTION:*** Nd:YAG (λ **= 532 nm**, 266 nm), 10 ns, 10 Hz, E_{max}= 0.1 – 1 J/pulse

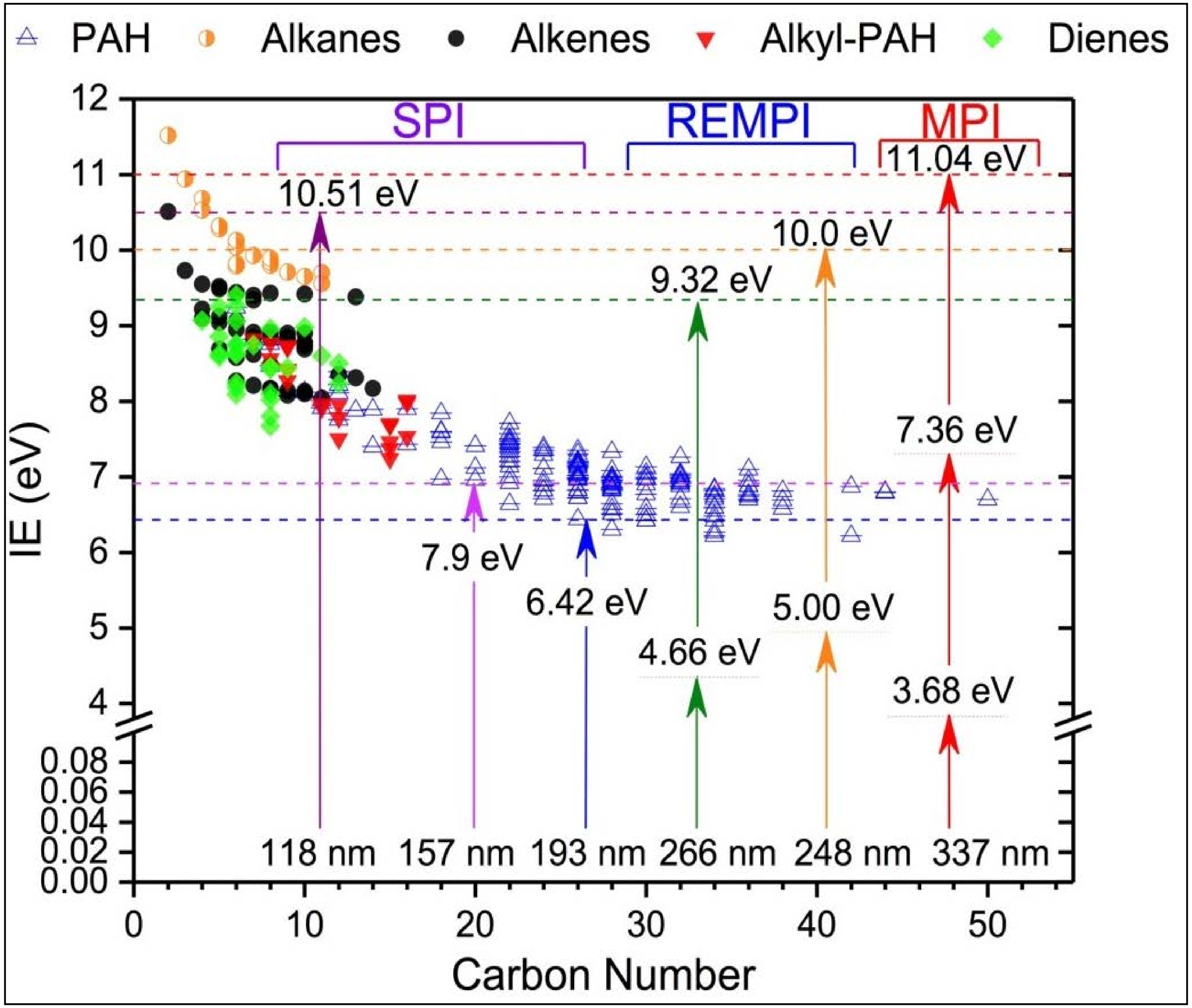
2 ***LASER IONISATION:***

- 4th harmonic Nd:YAG, λ**= 266 nm**, 10 ns, 10 Hz, E_{max}= 100 mJ/pulse
- **118 nm** source (9th harmonic Nd:YAG)
- **157 nm** F_2 excimer laser

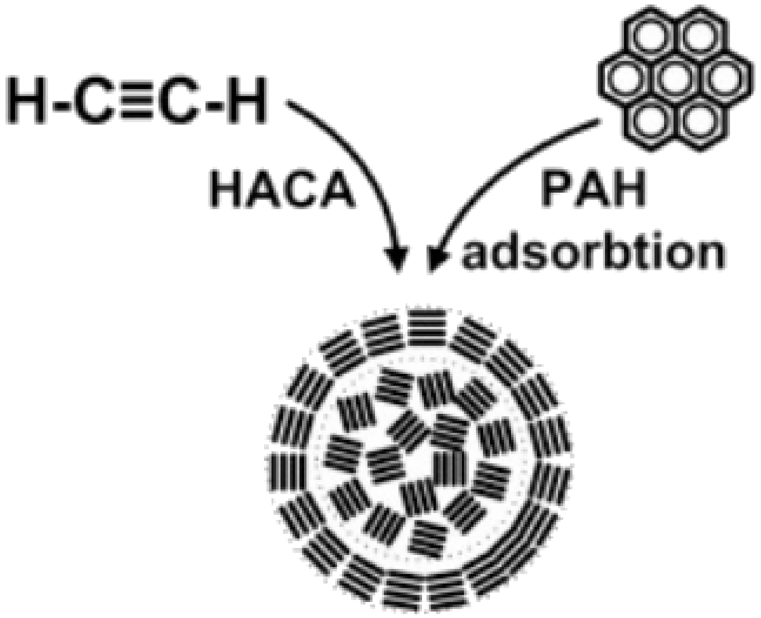
3 ***DETECTION:***

Reflectron Time-of-Flight Mass Spectrometer

Complementary ionisation schemes in the VUV

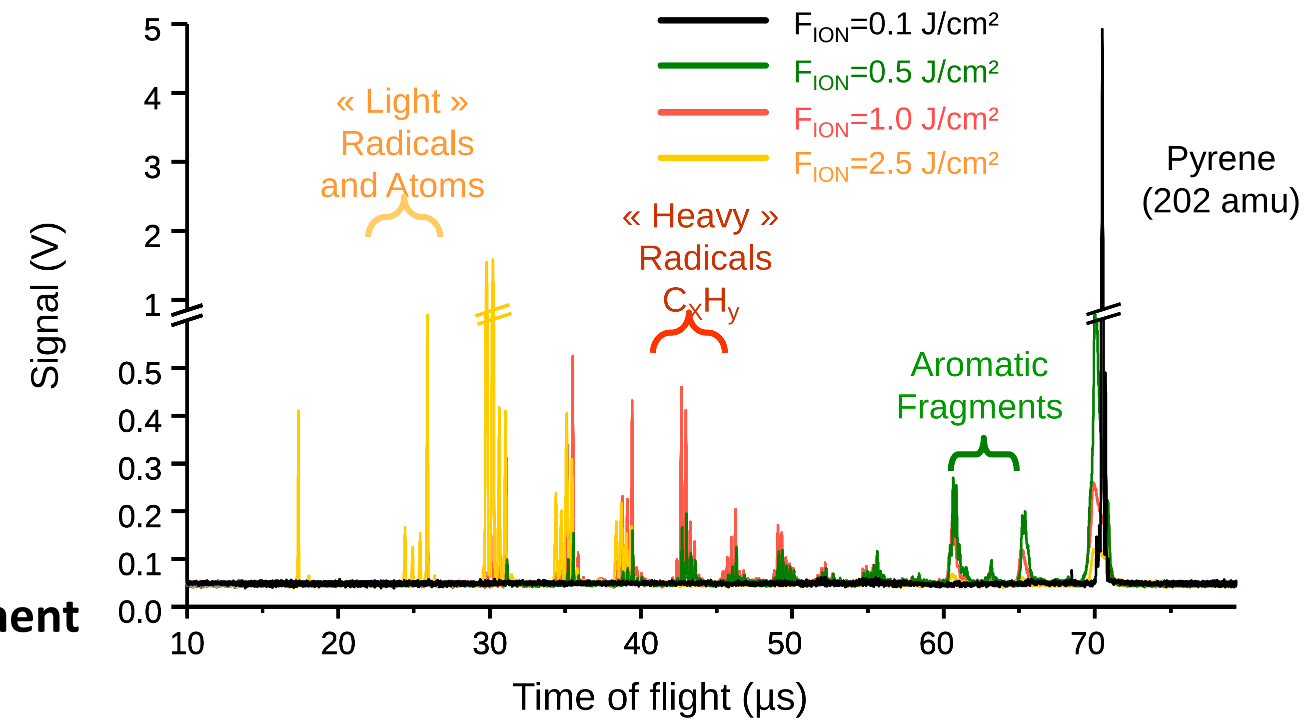


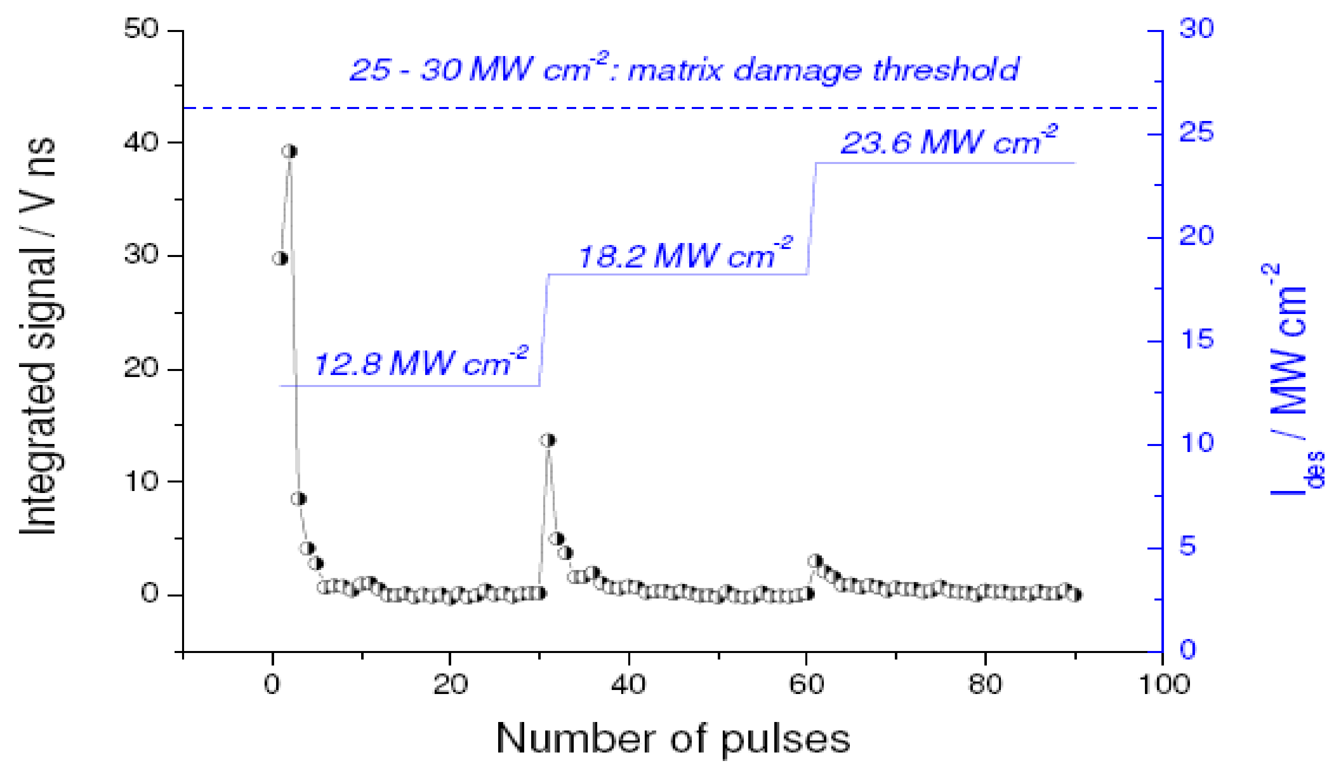
- **Soot surface composition**
- **Aromatics, PAHs**
- **Aliphatics and side-chains (alkanes, alkenes)**



Two-step Laser Mass Spectrometry Performances in Soot Analysis

- ✓ m/z detected typically up to 1000 Th (for soot)
- ✓ Mass resolution ~1000 … 20 000 with new high res instrument
- ✓ High sensitivity to PAHs … **LOD ~ 10 attomol per laser shot** (~10^{-5} ML) thanks to the **resonant absorption at 266 nm (REMPI)**
- ✓ Control the fragmentation degree
- ✓ Control the desorption depth
- ✓ (Semi)quantitative approach possible through external standard calibration, ionization cross section corrections





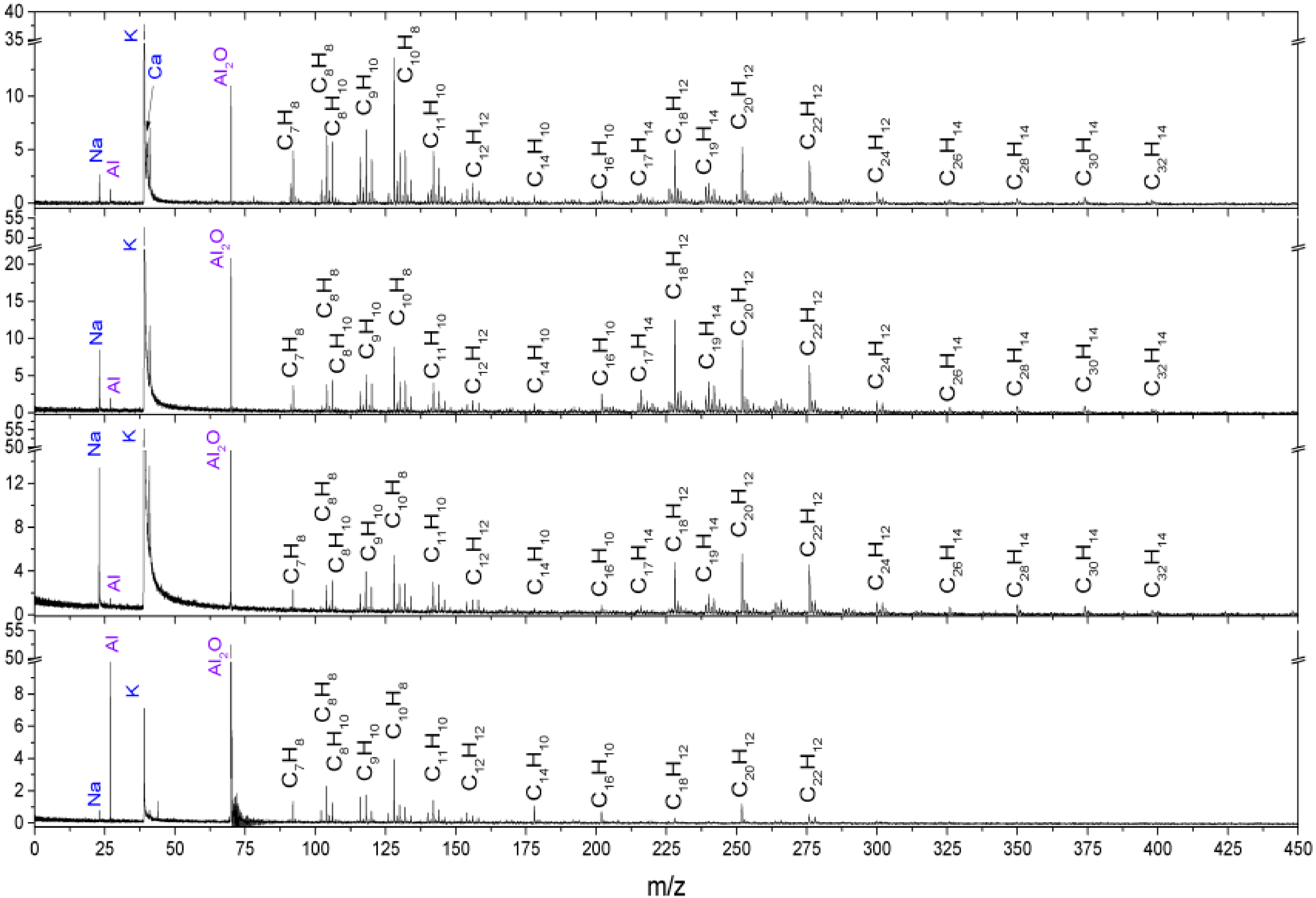
Pyrene / activated carbon, 9.52·10^{-8} mol/g, 600 m²/g

Faccinetto et al.,
Combust. Flame, **158**, 227 (2011)
Environ. Sci. Technol. **49**, *10510 (2015)*

Surface analysis of PEMs4Nano samples

R2PI at 266 nm

Spectra dominated by aromatic species



180-100 nm

100-56 nm

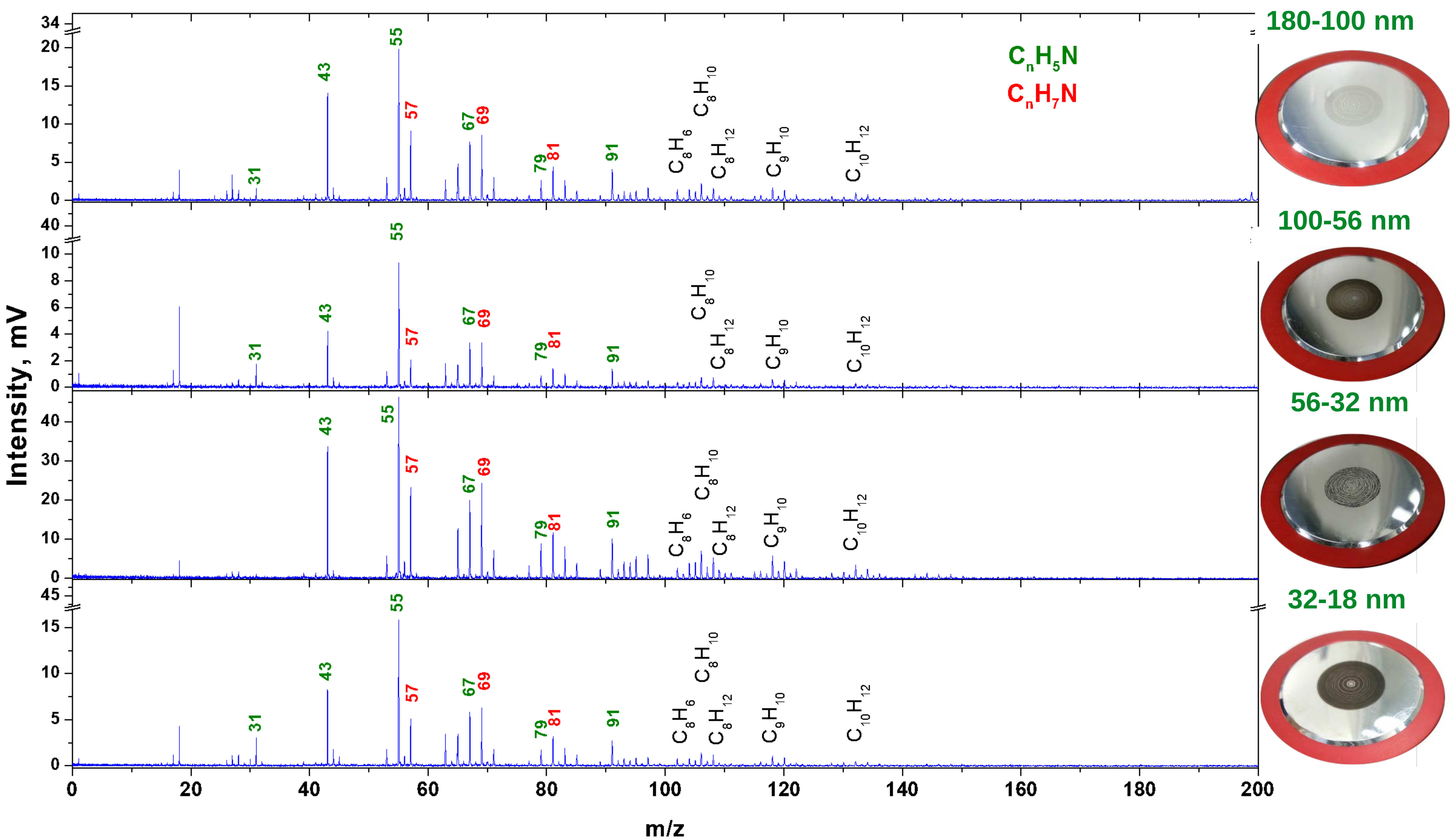
56-32 nm

32-18 nm

- Lower mass distribution for smallest particles

Surface analysis of PEMs4Nano samples

SPI at 157 nm

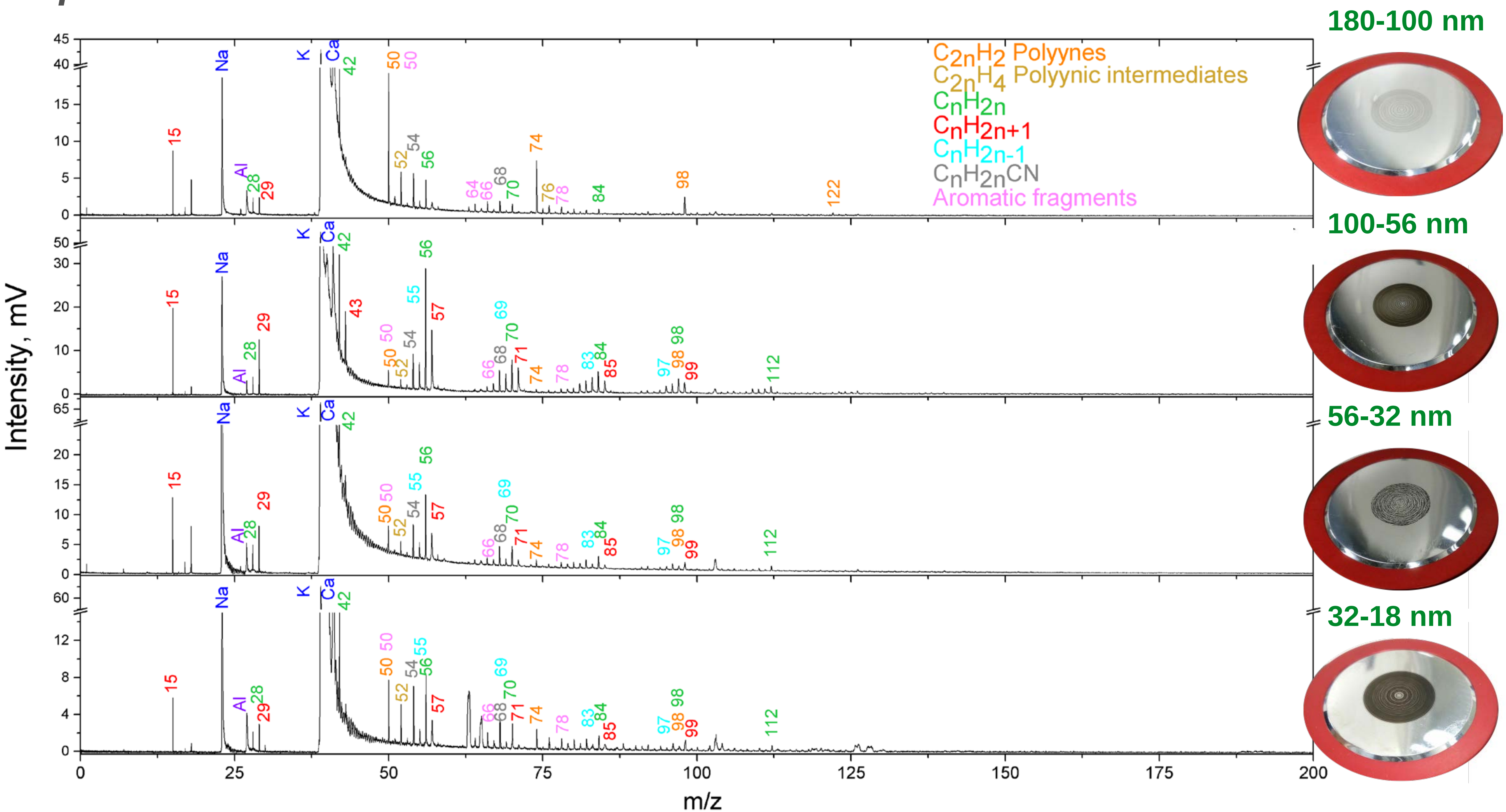


- Nitrogenated hydrocarbons are present

Surface analysis of PEMs4Nano samples

SPI at 118 nm

Spectra contain other chemical families

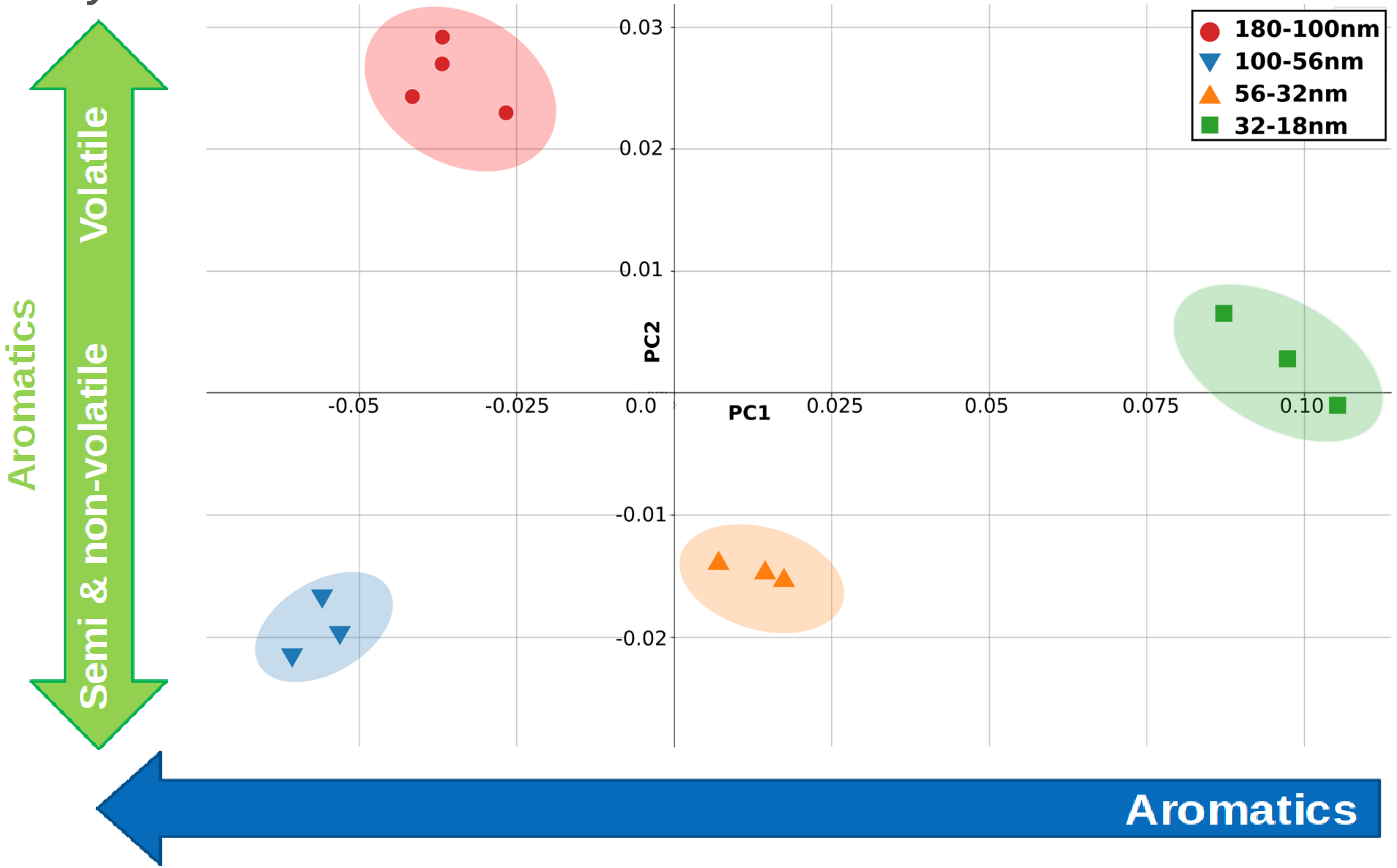


- Less obvious difference for smallest particles
- Need to use statistical analyses to differentiate

Surface analysis of PEMs4Nano samples

R2PI at 266 nm

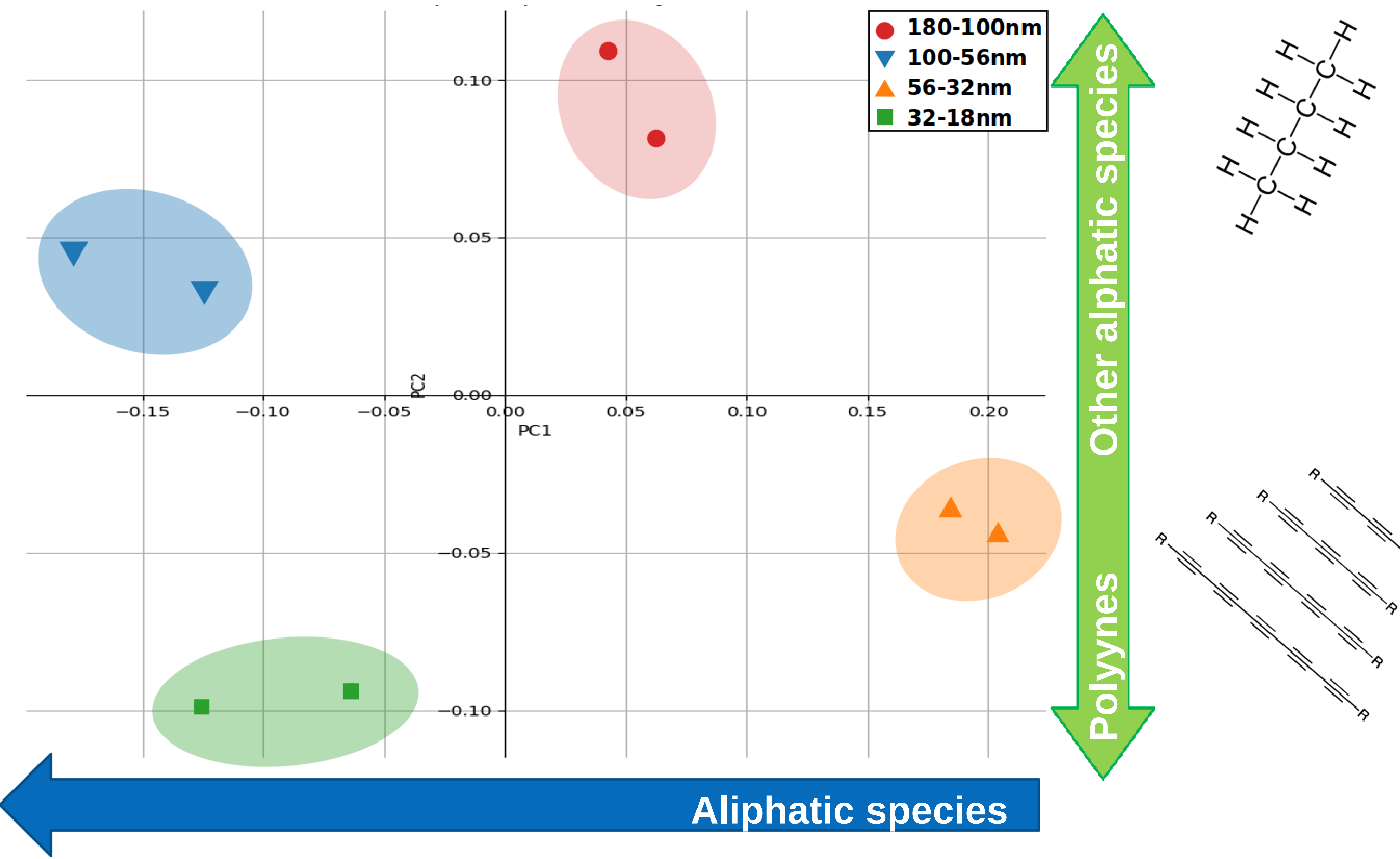
Principal Component Analysis



- **Chemically differentiate particles of different sizes**

Surface analysis of PEMs4Nano samples

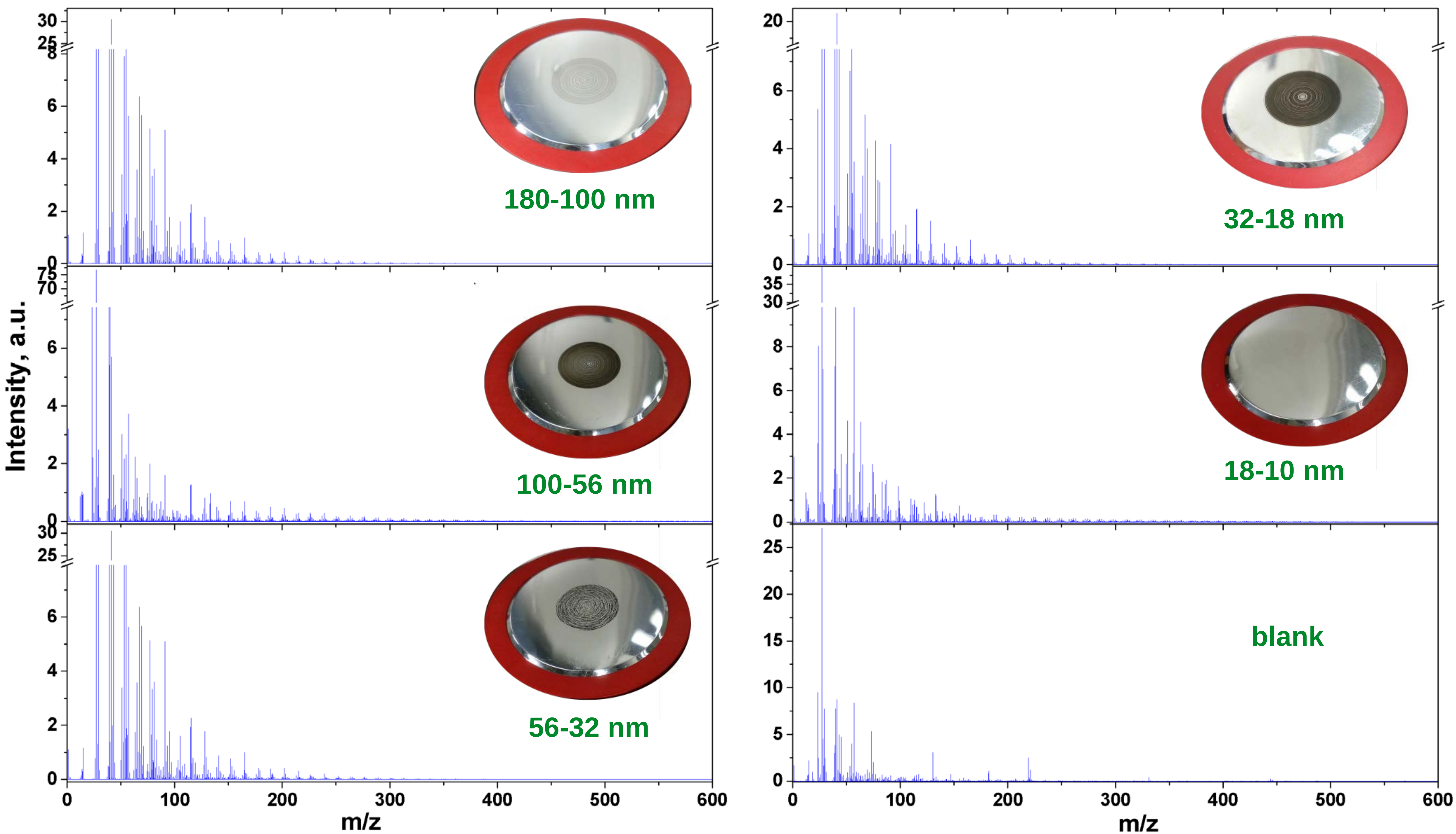
SPI at 118nm



- Chemically differentiate particles of different sizes

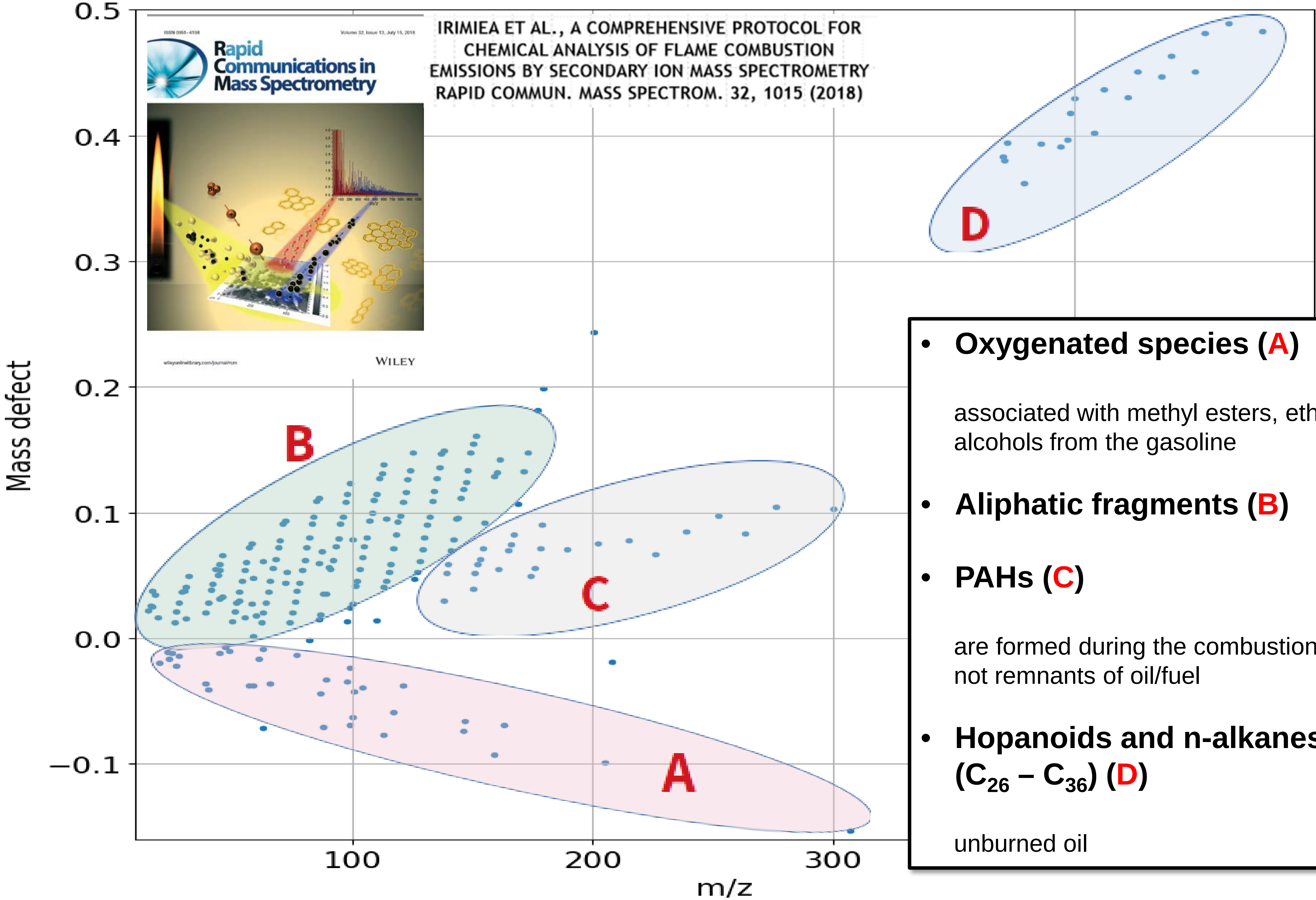
Surface analysis of PEMs4Nano samples

SIMS



- Spectra are dominated by aliphatic fragments

Mass defect for identification of various classes



- **Oxygenated species (A)**

  associated with methyl esters, ethers and alcohols from the gasoline

- **Aliphatic fragments (B)**

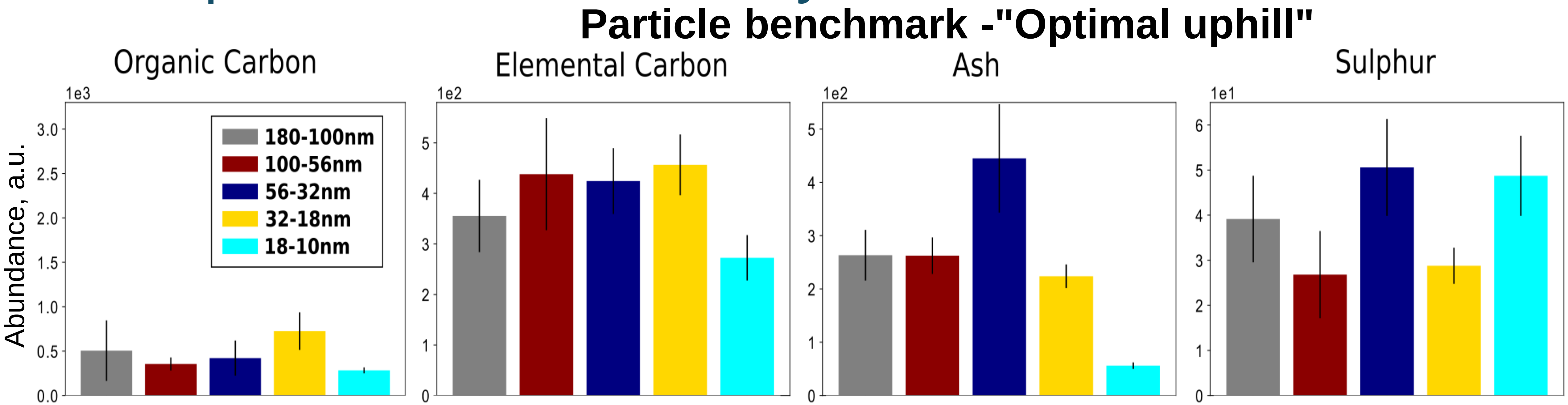
- **PAHs (C)**

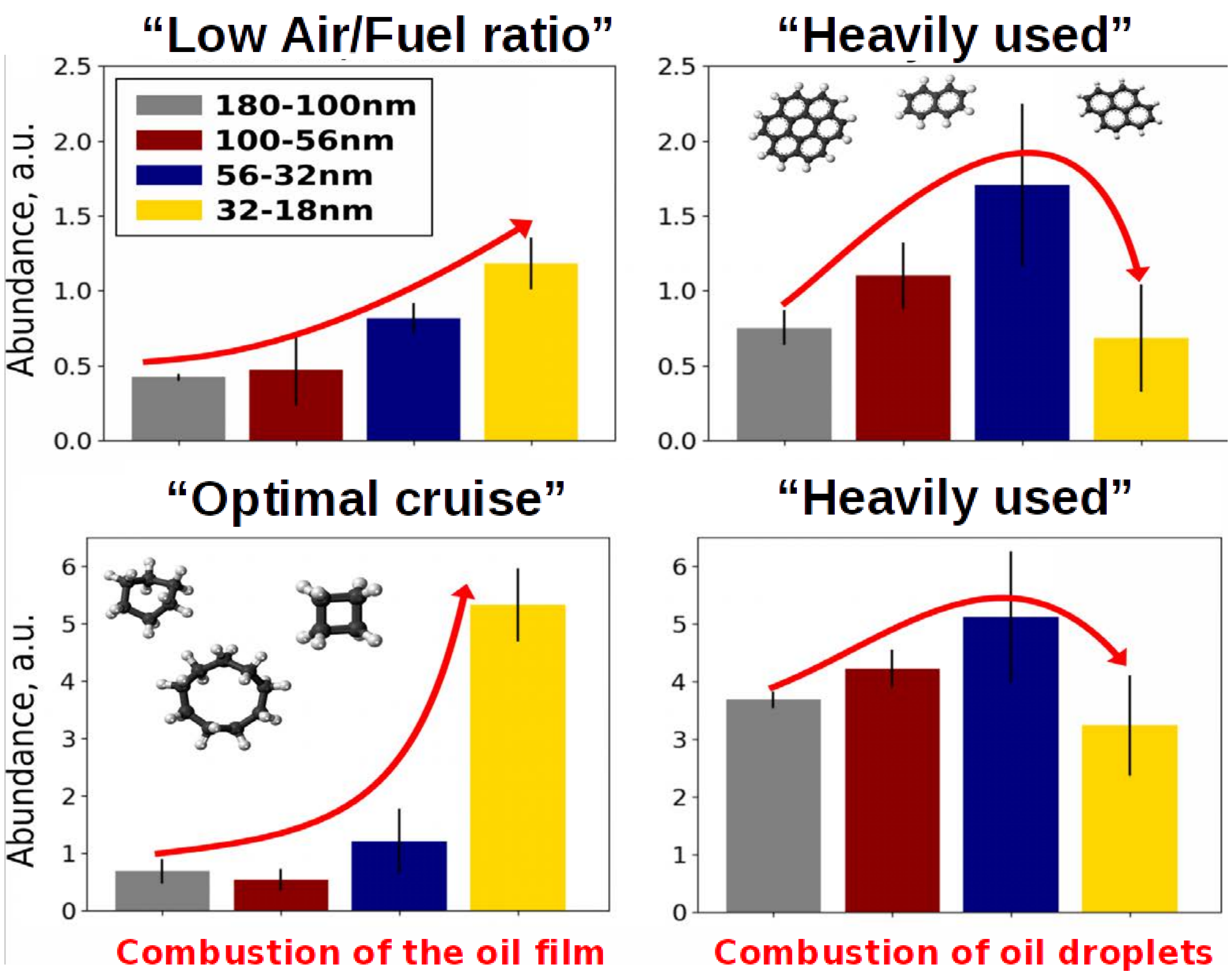
  are formed during the combustion and are not remnants of oil/fuel

- **Hopanoids and n-alkanes (C_{26} – C_{36}) (D)**

  unburned oil

Size-dependent chemical analysis





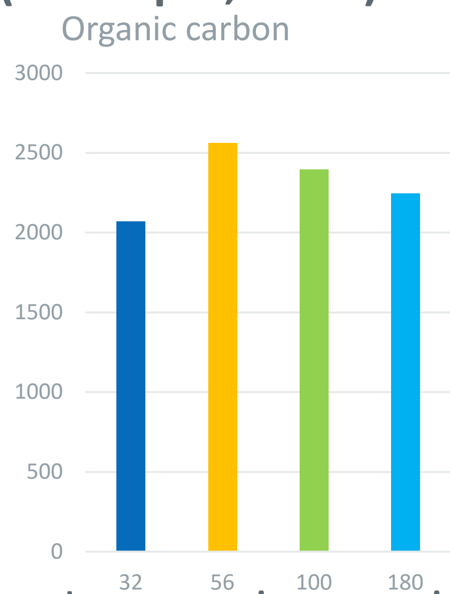
Clear trends in **size** and **source** have been identified for:

- **Cycloalkane and bicycloalkane fragments** (C_nH_{2n-3}) - markers of lubricating oil
- **Polycyclic aromatic hydrocarbons (PAH)** - building blocks of soot particles

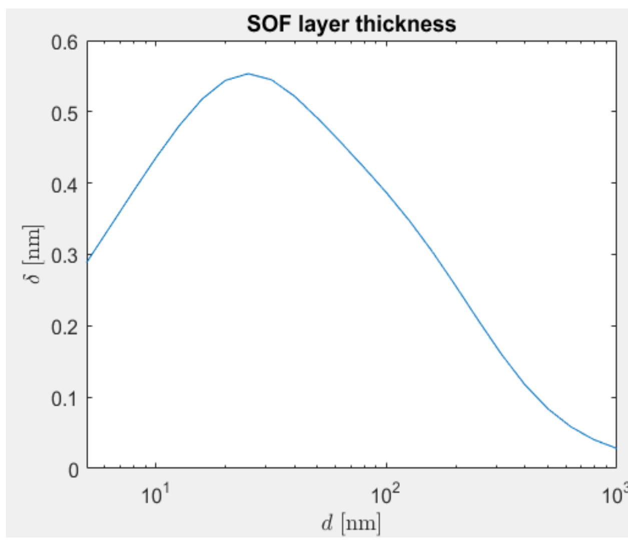
Size variation by chemical category delivered as key input to the Model Guided Application (U.Cam + CMCL)

MGA: chemical characterisation

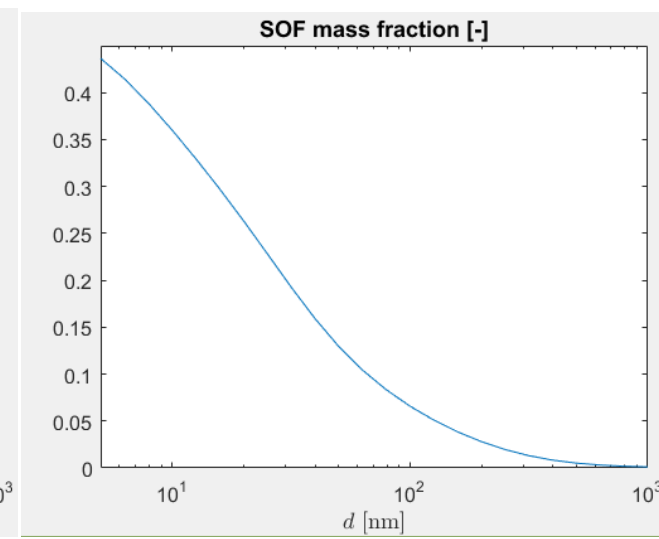
Operating point (2000 rpm, 8 bar)



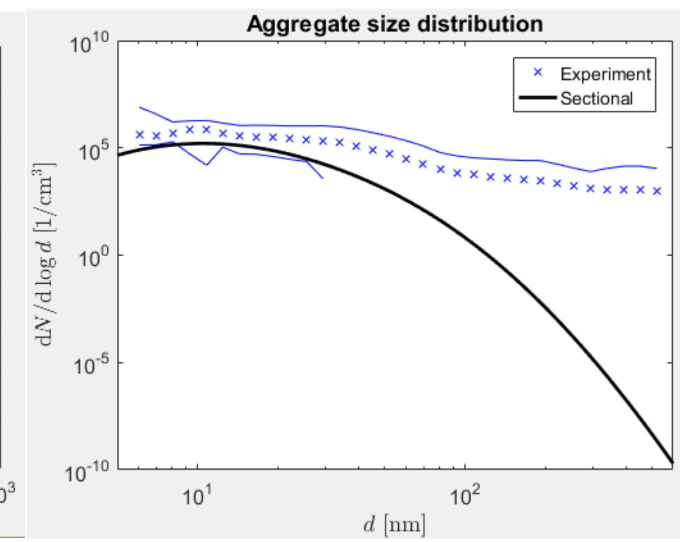
- Increase in organic carbon from 32 – 56, then starts to decrease
- Decrease in elemental carbon as size increases



- Increase in SOF thickness up to about 30 nm before decreasing
- Trend agrees with ULL's results, assuming the laser technique has a fixed penetration depth



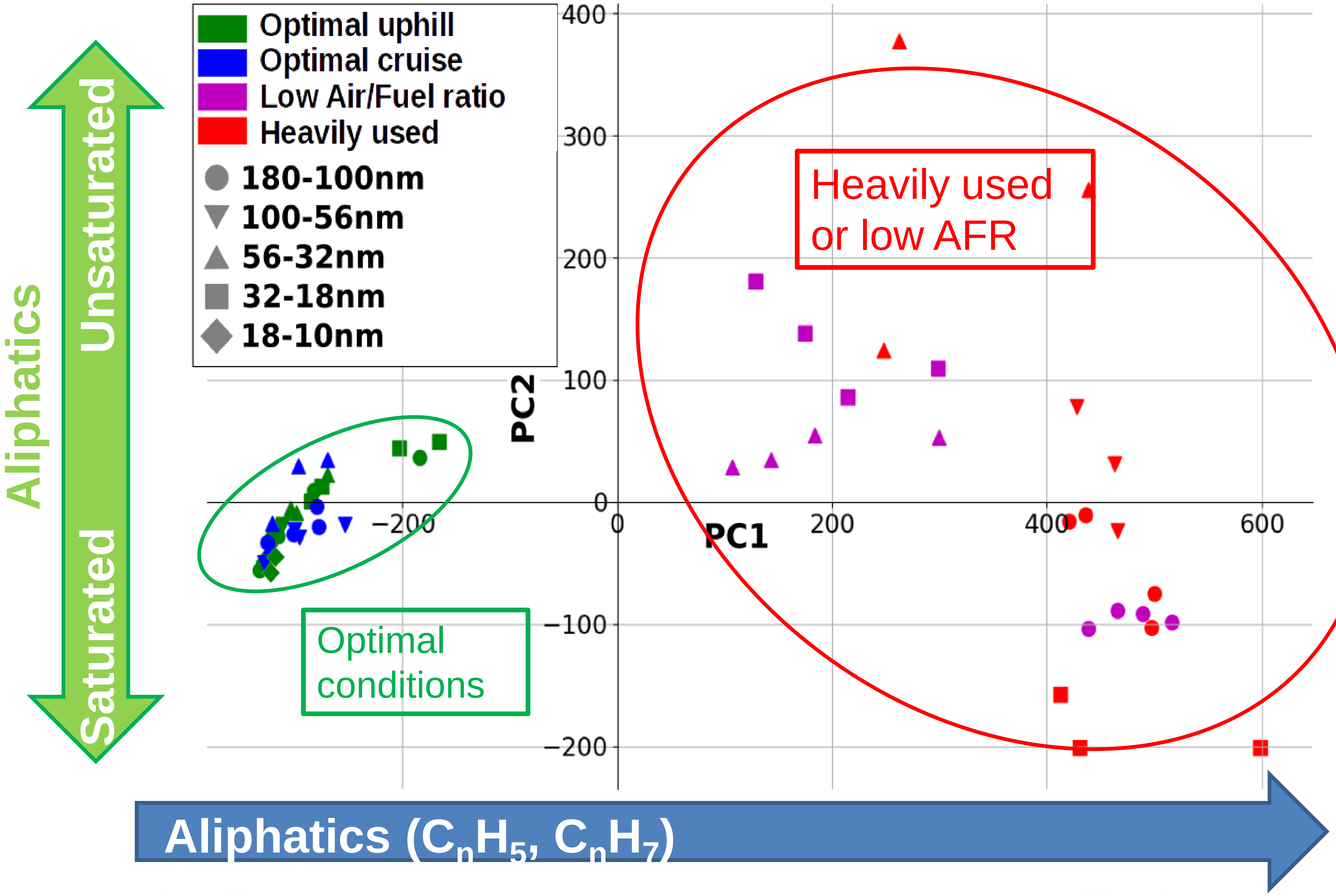
- Decreasing SOF mass fraction with size (in line with findings in the literature)



- Size distribution explains the position of the peak in the SOF layer thickness plot
- Condensation of SOFs is collision based, roughly proportional to the number density

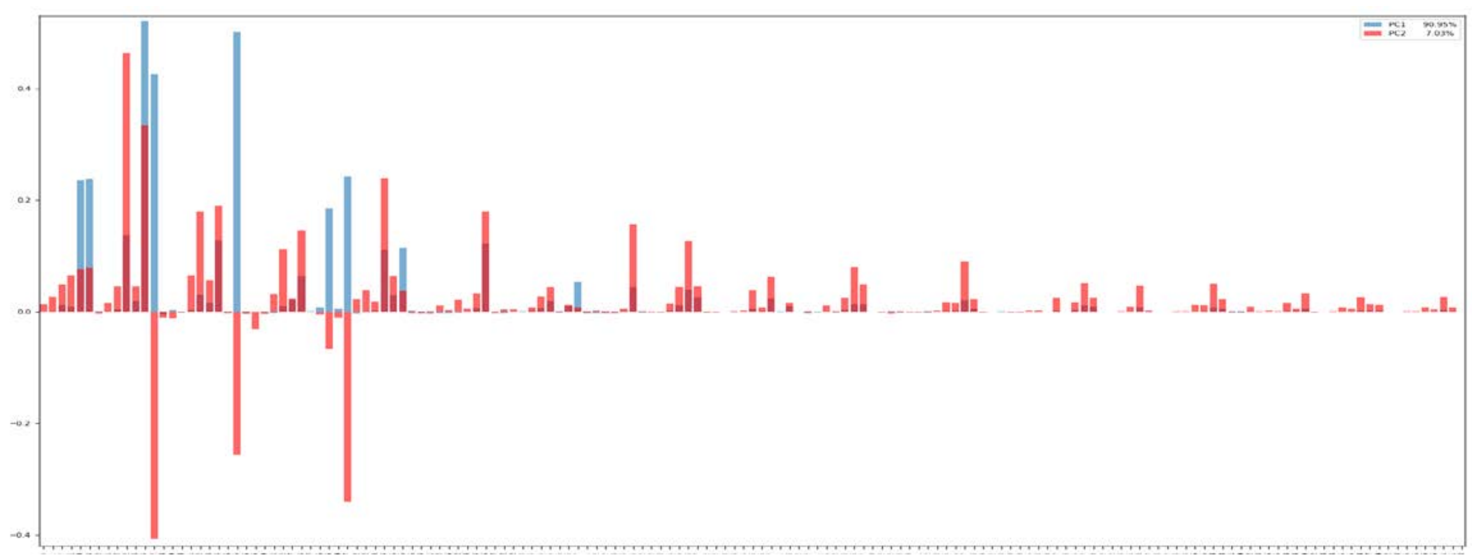
Regime discrimination

SIMS



Identification of chemical markers to discriminate particles produced in different engine conditions as benchmark for MGA

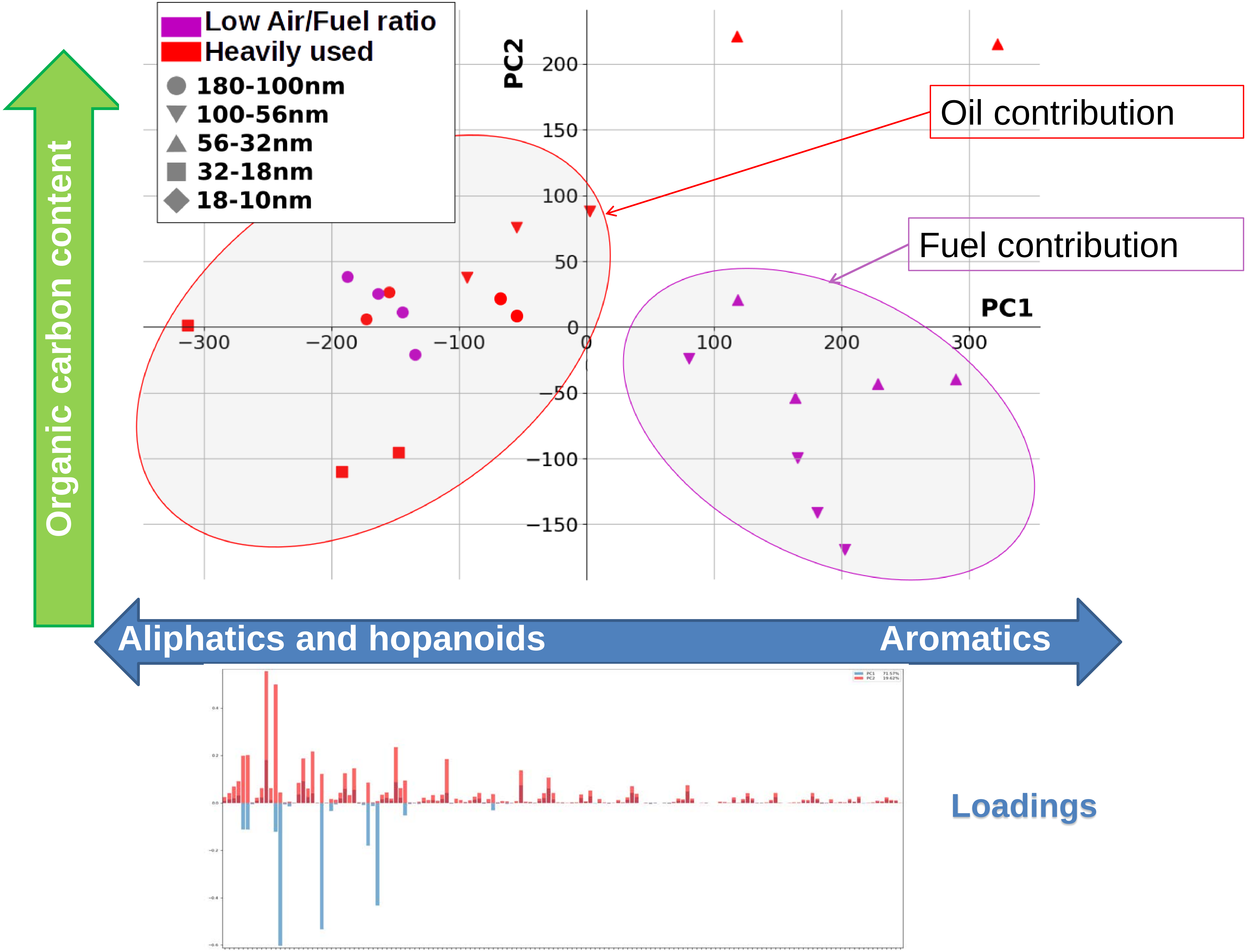
e.g.: aliphatics discriminate optimal from non-optimal regimes



Loadings

Source discrimination

SIMS



Conclusions

- The combination of **L2MS**, **SIMS** and **PCA** allows determination of detailed molecular level surface chemical composition of soot particles.
- The use of **size-selective** sampling allowed us to chemically characterise surface chemistry of particles down to 10 nm.
- Identification of key chemical markers, coupled with powerful PCA statistics, allowed discrimination of:
  - **Gasoline-specific** (PAHs, phenol, nitro-phenol)
  - **Lubricant-specific** (Hopanoids, steranes and cycloalkanes)
  - **Engine-specific** (metals and metal oxides)
- By identifying marker species, we have clearly discriminated particles by **source**, **particle size** and **engine regime**

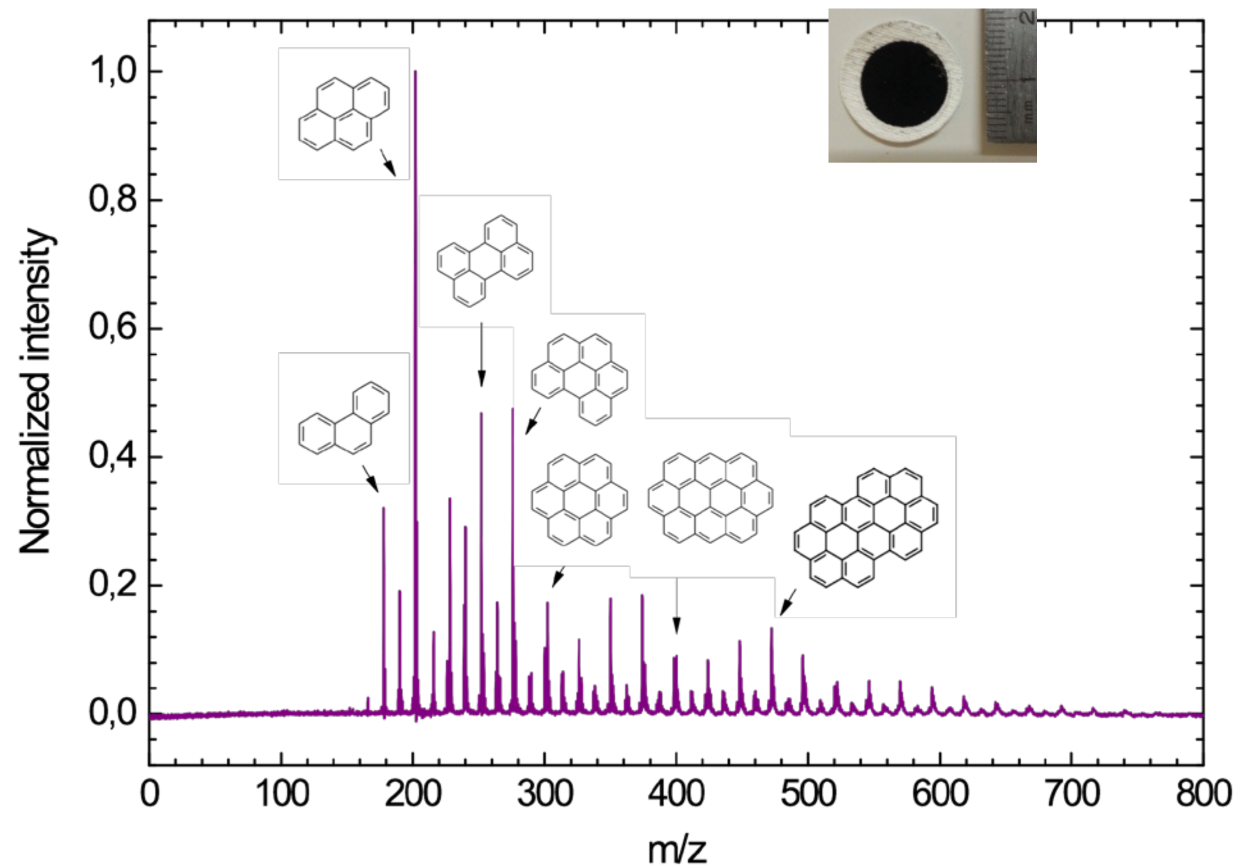
Thank You !

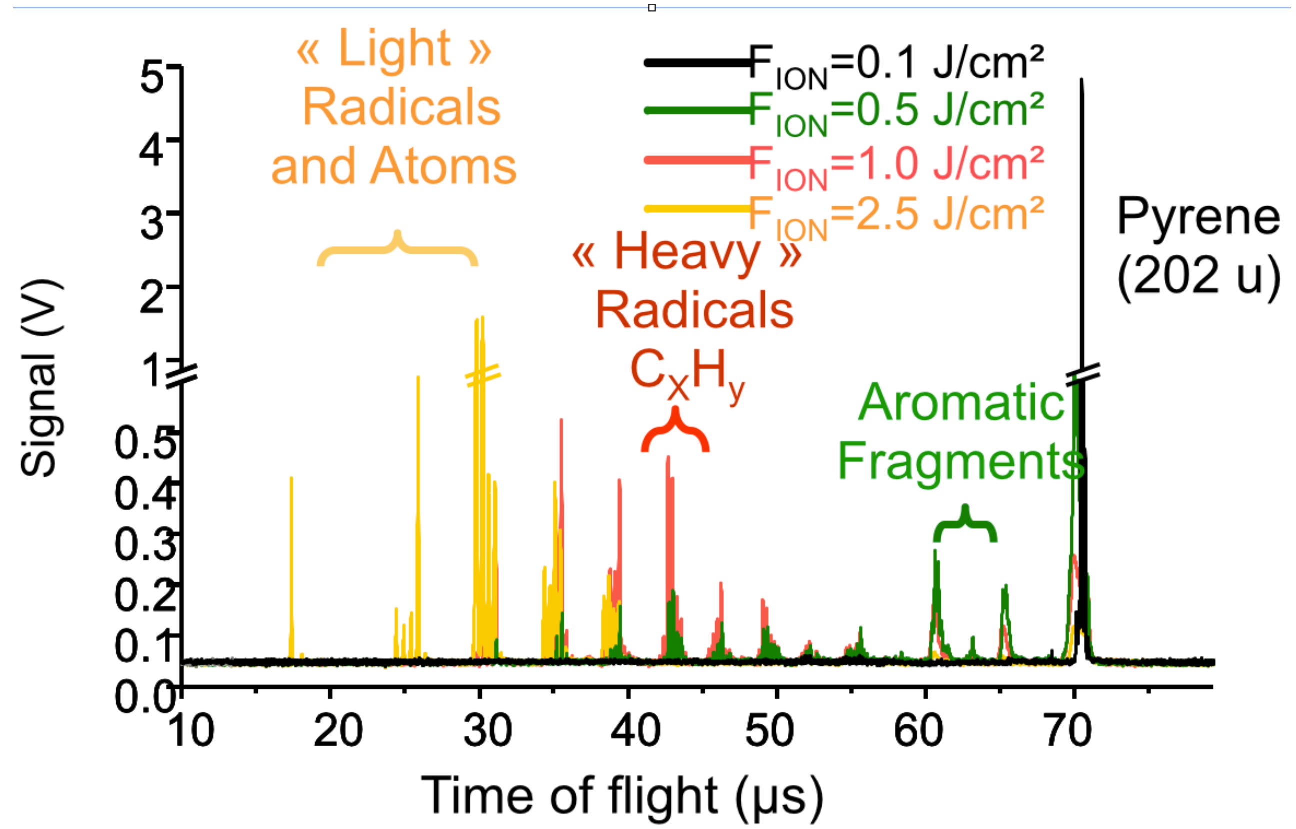
L2MS performance

- Mass resolution m/Δm ≈ 1000
- Masses detected typically up to m/z 1000 (for soot)
- High sensitivity to PAHs: LOD ~ 0.1 fmol per laser shot (REMPI 266 nm)

- Control the fragmentation degree
- Control the neutral / ion formation
- (Semi)quantitative approach possible through external standard calibration
- Surface analysis

desorption: 532 nm - ionisation: 266 nm

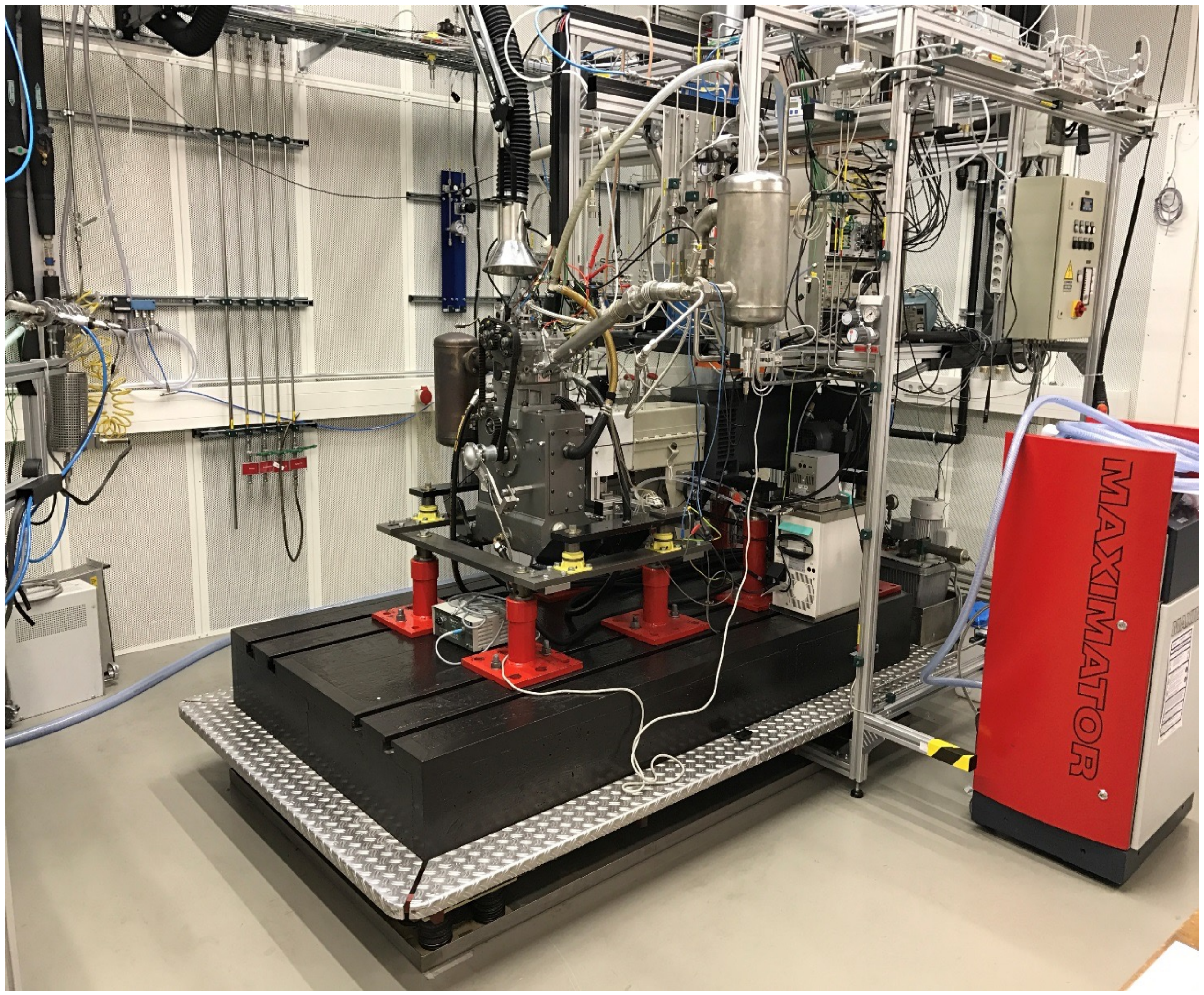




Faccinetto et al. 2008, 2011, 2015

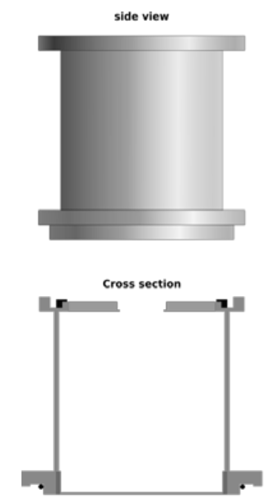
Particulate matter collection campaign

BOSCH Invented for life PhLAM HORIBA Scientific TSI UNDERSTANDING, ACCELERATED



- Laboratory single cylinder test engine (Bosch)

- Comprehensive collection of particulate matter



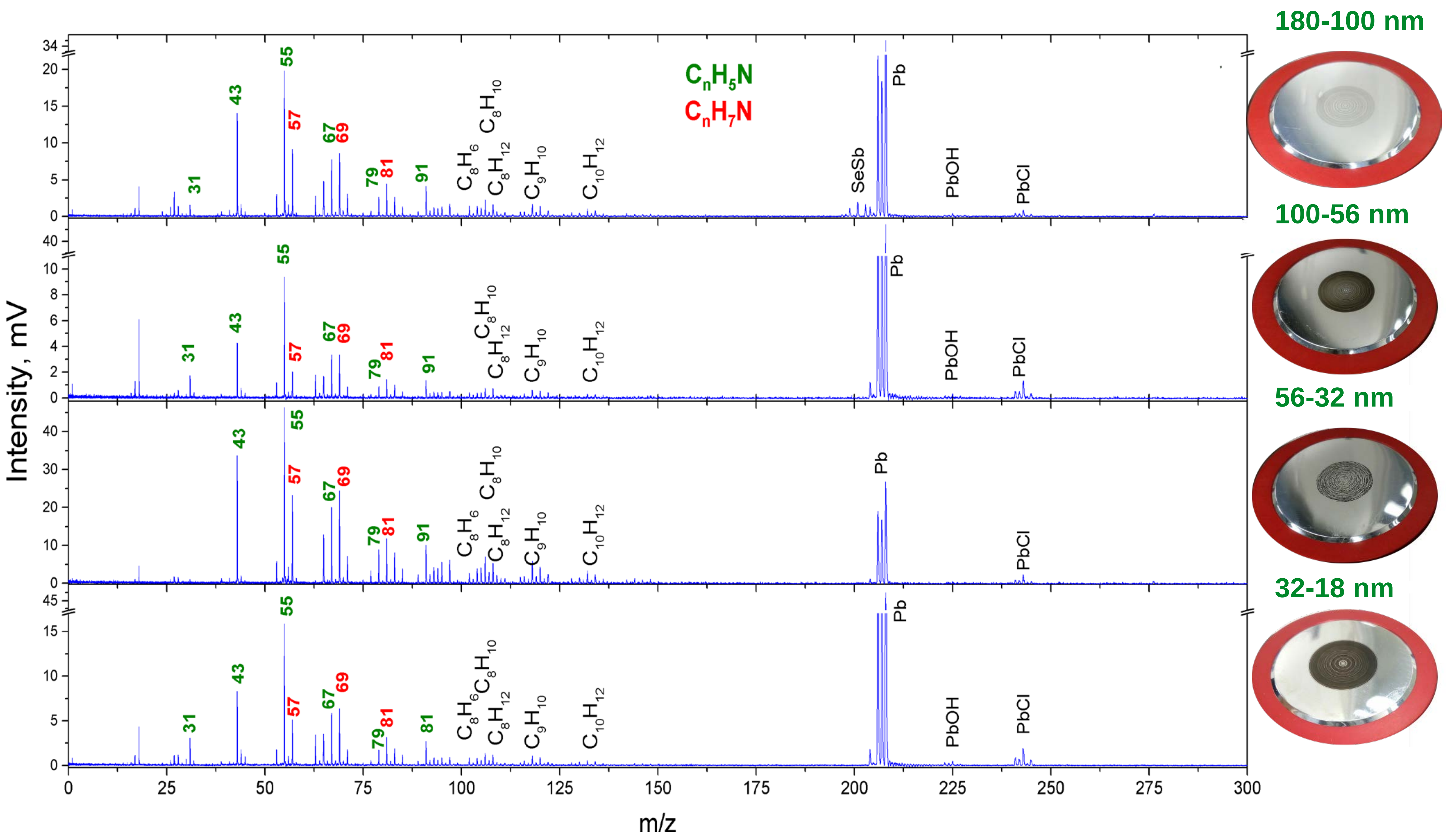
borosilicate filters

- Size-selected collection methods (down to 10 nm)

nanometre aerosol sampler **and** **nanoMOUDI (TSI)**

Surface analysis of PEMs4Nano samples

SPI at 157 nm



- Nitrogenated hydrocarbons are present

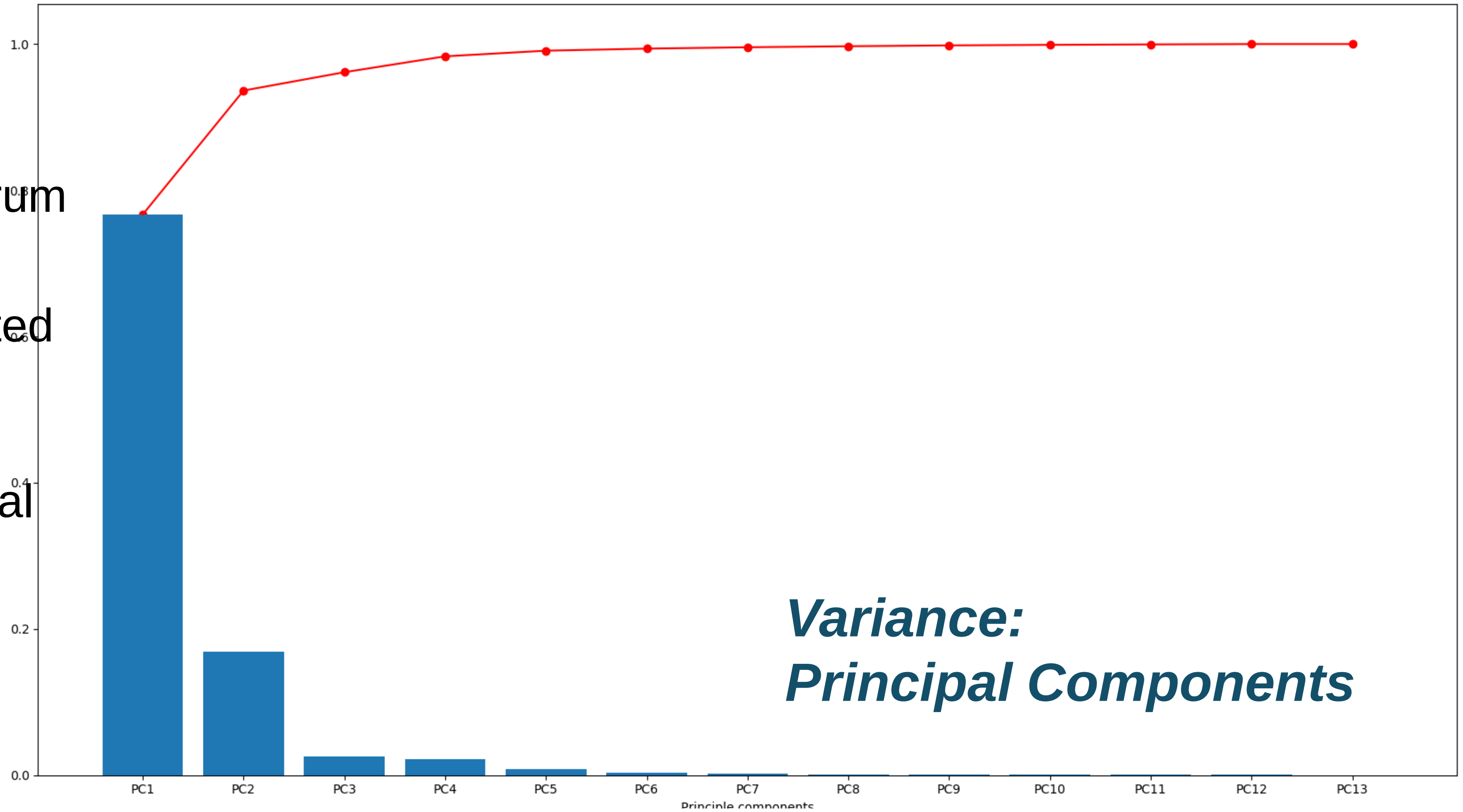
Surface analysis of PEMs4Nano samples

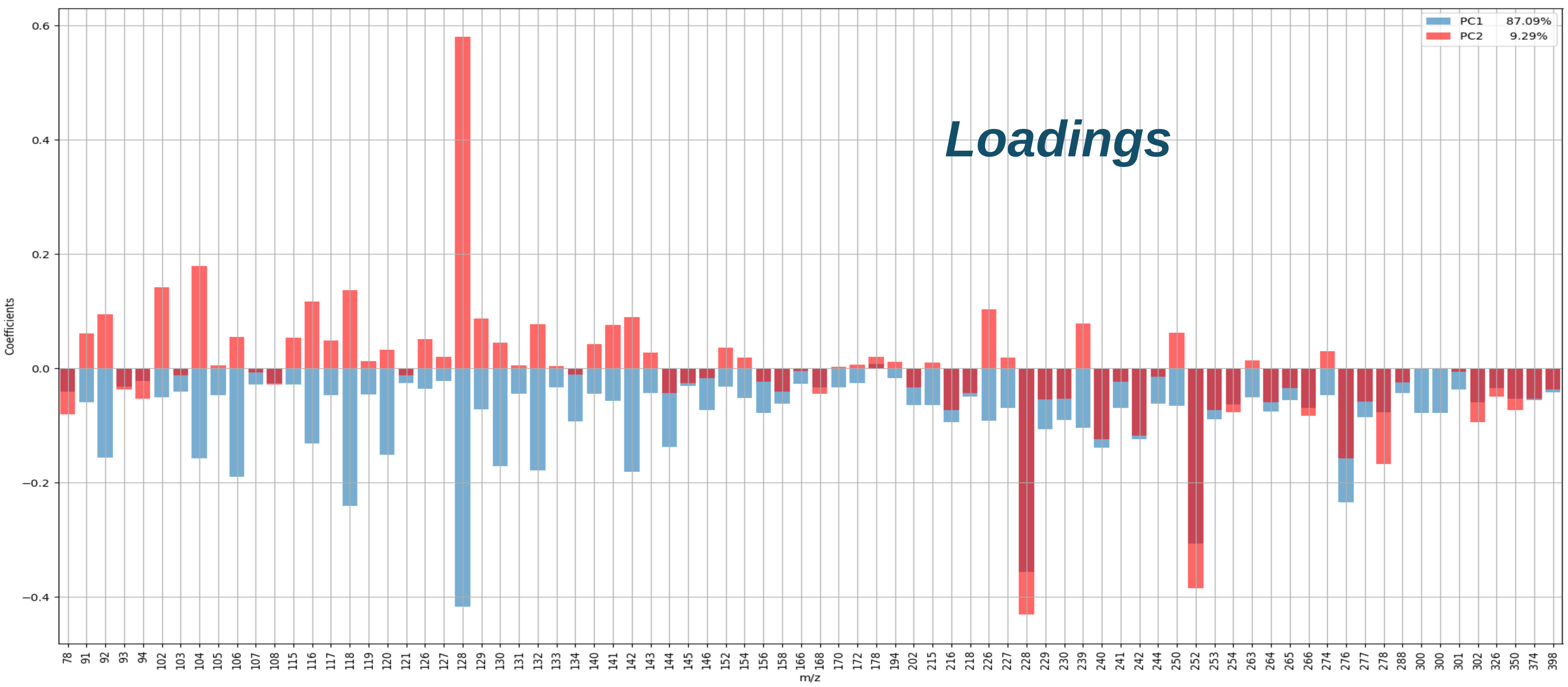
R2PI at 266 nm

Principal Component Analysis

- Peak areas compared within a spectrum (variables)
- Variance between all spectra calculated (orthogonal transformation)

- Loading per mass unit allows chemical attribution of Principal Components



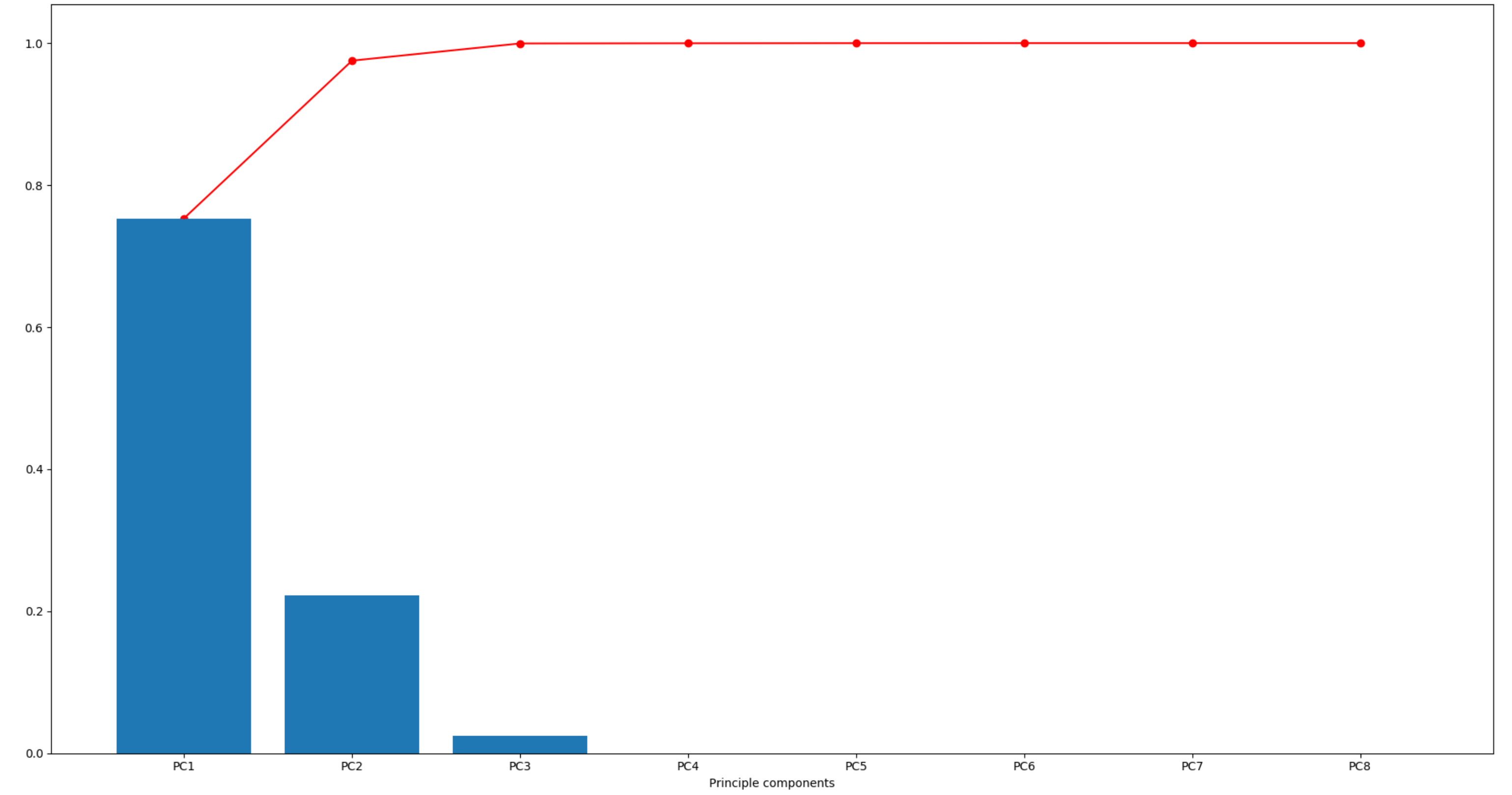


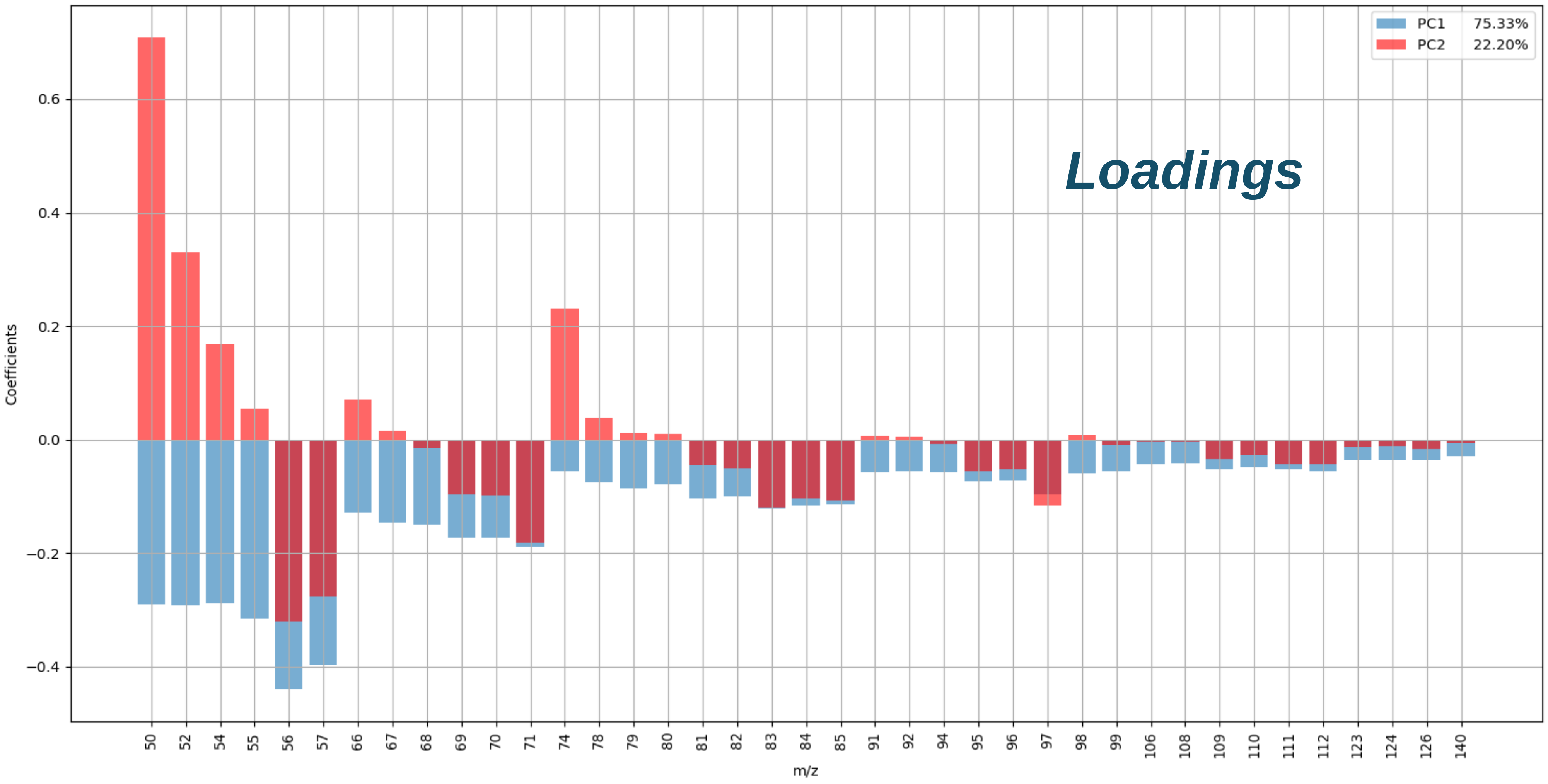
Surface analysis of PEMs4Nano samples

SPI at 118 nm

Principal Component Analysis

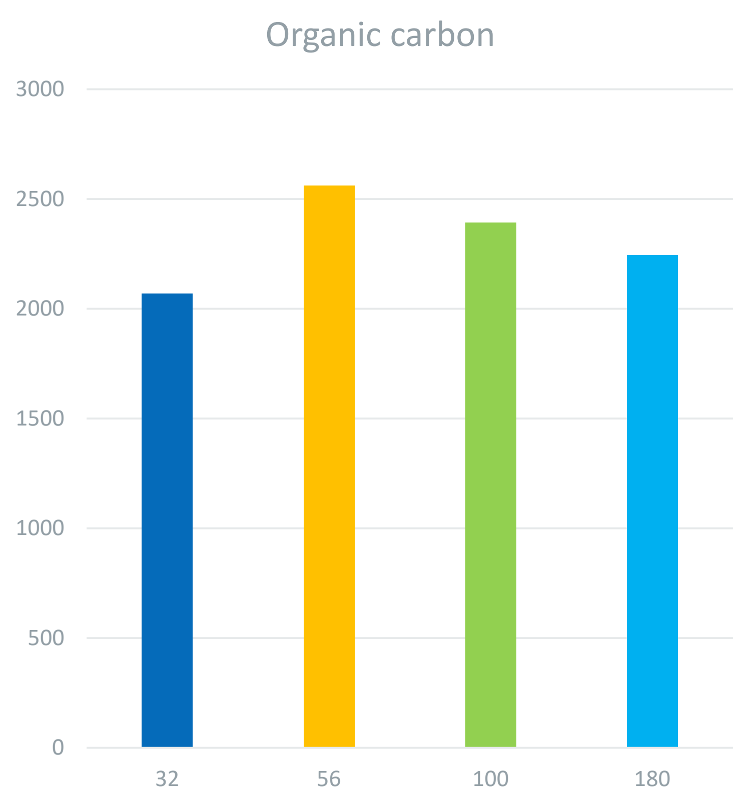
- Peak areas compared within a spectrum (variables)
- Variance between all spectra calculated (orthogonal transformation)
- Loading per mass unit allows chemical attribution of Principal Components

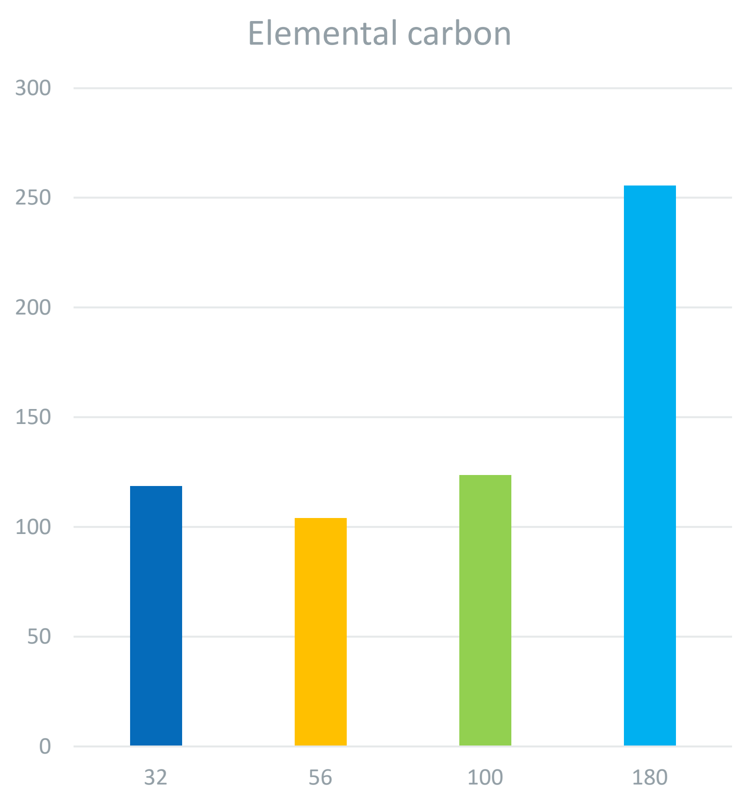




MGA: chemical characterisation

- Data from Uni of Lille's measurements campaign at Bosch SCRE





Size-resolved chemical characterisation

- Experimental technique used focuses on surface concentrations
- MGA tracks the thickness of the SOF layer in addition to SOF mass fraction
- It is assumed that the experimental technique only characterises the particles up to a certain depth and the results are not representative of the bulk content