European Commission

Material Characterisation of vehicle-emitted fine and ultrafine particles

S. Valentini[1], C. Ferrarese[1,2], D. Manara[1], D. Mehn[1], A. Valsesia[1], J. Ponti[1], N. Fonseca[2], G. Schirinzi[1], G. Martini[1,*]

[1] *European Commission, Joint Research Centre (JRC), Via Enrico Fermi, 2749, I - 21027 Ispra (VA), Italy*

[2] *ETSI Minas y Energía, Universidad Politécnica de Madrid, c/Rios Rosas 21, 28003 Madrid, Spain*

PROJECT BACKGROUND

Micro-metric and sub-micrometric particles emitted from modern light-duty (LDV) and heavy-duty vehicles (HDV) were characterised in the frame of the **Market Surveillance of vehicle emissions** (introduced in **European Commission Regulation 858 (2018)** [1]). This work is part of the Transport and Mobility Portfolio of the **European Commission's Joint Research Centre** (EC JRC).
Vehicle emission tests were performed at the EC JRC **Vehicle Laboratories (VELA)**.

REGULATION (EU) 2018/858 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 30 May 2018

on the approval and market surveillance of motor vehicles and their trailers, and of systems, components and separate technical units intended for such vehicles, amending Regulations (EC) No 715/2007 and (EC) No 595/2009 and repealing Directive 2007/46/EC

(Text with EEA relevance)

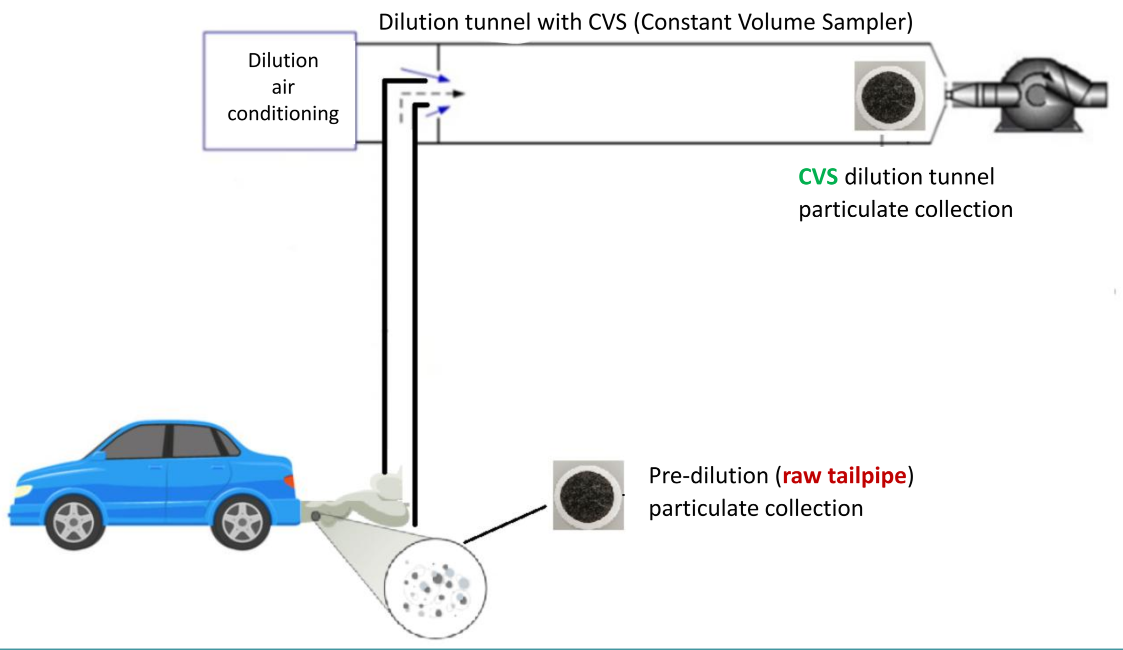
COMMISSION REGULATION (EU) 2017/1151

of 1 June 2017

supplementing Regulation (EC) No 715/2007 of the European Parliament and of the Council on type-approval of motor vehicles with respect to emissions from light passenger and commercial vehicles (Euro 5 and Euro 6) and on access to vehicle repair and maintenance information, amending Directive 2007/46/EC of the European Parliament and of the Council, Commission Regulation (EC) No 692/2008 and Commission Regulation (EU) No 1230/2012 and repealing Commission Regulation (EC) No 692/2008

(Text with EEA relevance)

METHODOLOGY



Internal Combustion Engine vehicles exhaust **particulate samples** collected on filters at the:

- **CVS** dilution tunnel (according to **European Commission Regulation 1151 (2017)** [2])
- **Raw tailpipe**

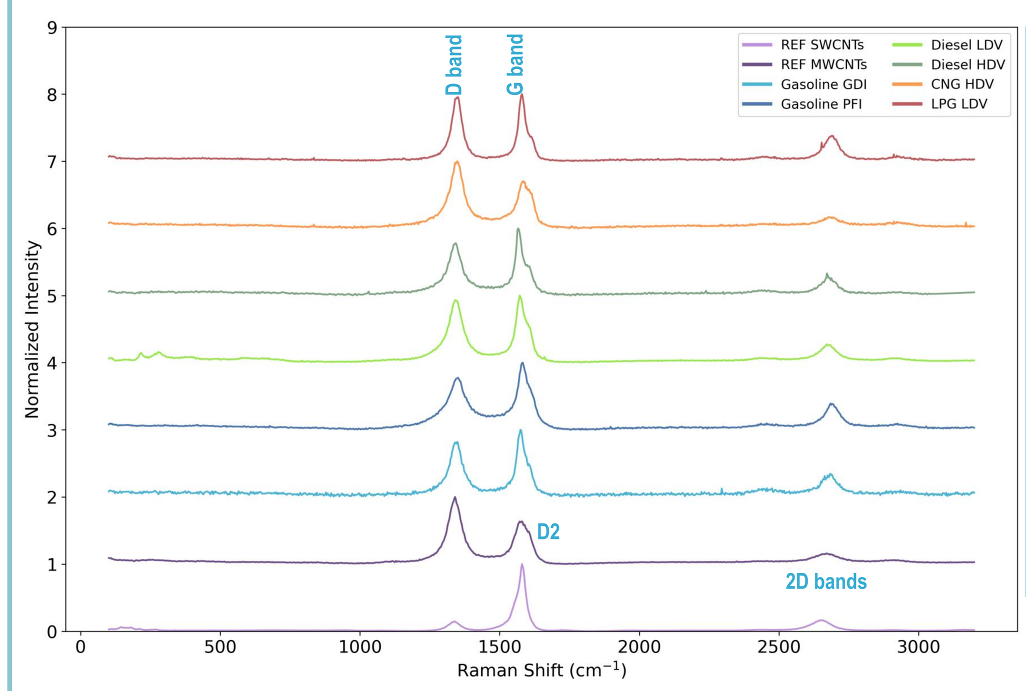
Optical microscopy coupled with **Raman spectroscopy** of micro- and sub-micro metric particles emitted by both light- and heavy-duty vehicles (LDV and HDV) powered by different fuels.

Analysis complemented by **Transmission Electron Microscopy** (TEM) on selected samples with peculiar features.

- Large database of more than **200 Raman spectra**.
- **Principal Component Analysis (PCA)**: identification and characterization of underlying patterns and variances among the spectra to highlight compositional differences.
- Clusters of spectral features giving insight into the **chemical nature** of each sample based on the recorded Raman spectra.

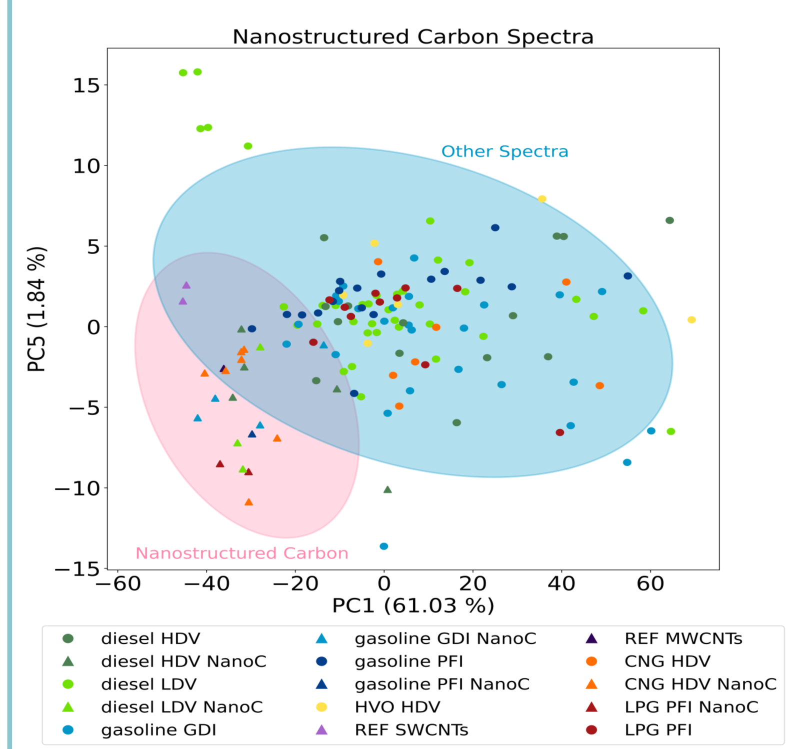
RESULTS

FOCUS: Multi-Walled Carbon Nano Tubes (MWCNTs) in raw tailpipe samples



Raman Spectroscopy

D (defective graphite) and G (ordered graphite) bands systematically observed
❖ **black carbon**-dominated samples
❖ variable relative intensities and presence of other modes or sub-peaks depending on **fuels/technologies/sampling point**
❖ **raw tailpipe samples** showed D2 (as a shoulder of G band, 1610 - 1625 cm^{-1}) and 2D (~2600 - 2700 cm^{-1}) bands typical of **MWCNTs**

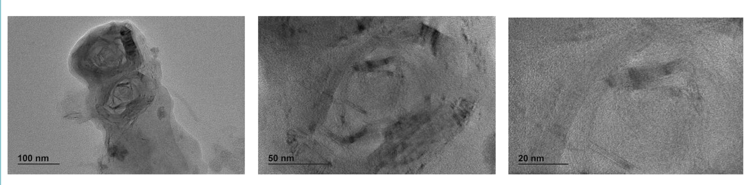


PCA

PC5: able to **cluster carbon nanostructures data** points.

Spectra with **MWCNT-like features** measured on **raw** samples of practically all vehicle types, fuels and injection technologies.

MWCNT can form during combustion in internal combustion engines in the presence of high temperatures, pressures and metal catalysts [3].



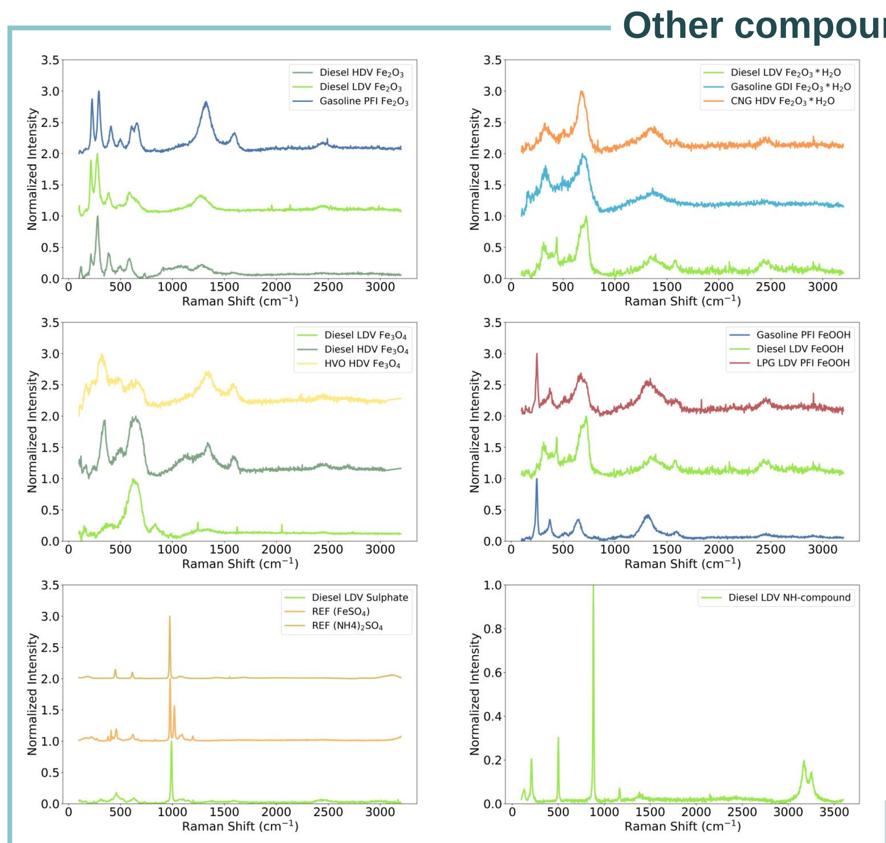
TEM

Presence of sub-micrometric objects in the particulate samples that also displayed Raman spectra very close to those of reference CNTs (likely actually present in these particulate samples).

All analyses showed **MWCNT** features on **RAW** tailpipe samples only (before CVS).

Samples collected **after CVS dilution** did not exhibit any sign of MWCNT presence

Other compounds and overall results

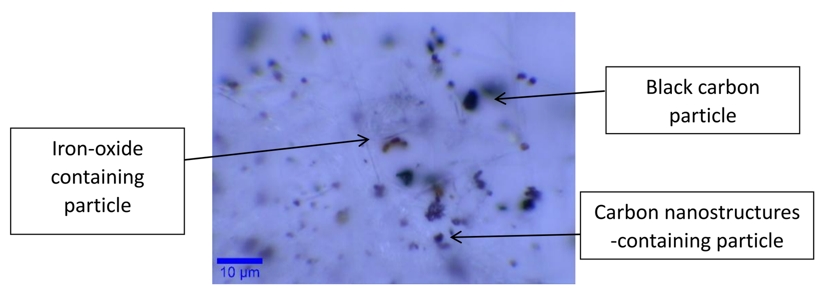


Non-carbonaceous Raman spectra

Iron oxides (Fe_xO_y – from catalytic converters) in various chemical compositions

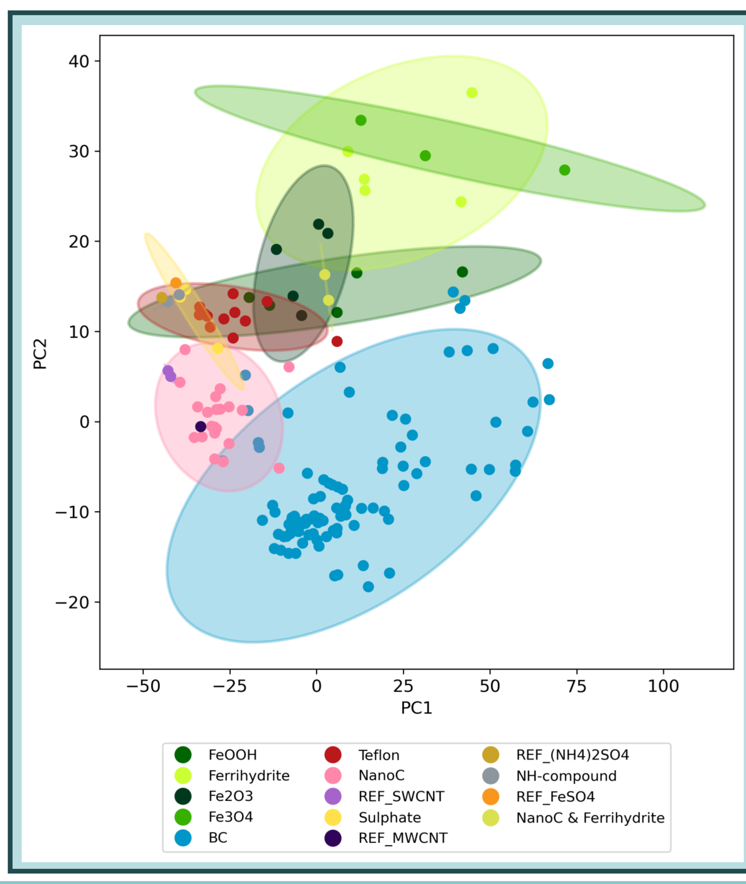
Ammonium sulphate ($(NH_4)_2SO_4$ can form in Selective Catalytic Reduction system [4]

Nitrogen compounds in samples collected from Diesel HDV (probably coming from the SCR urea)



Optical microscopy

Visually relate the nature of some particles with their optical microscope images on the micrometric scale:
❖ black carbon
❖ nano-crystalline carbon agglomerates (more translucent)
❖ iron oxide (reddish)



PCA PC1-PC2 score plot shows **excellent clustering**, effectively separating the various compounds.

PCA gives a deeper indication of the capability of the current Raman analysis to distinguish between the **different compositional characteristics of particulate matter**.

PCA helps to identify different features in **black carbon** originating from **different types of engine or fuel**.

Clusters relating to **other chemical species** (e.g. **MWCNTs, iron oxides, sulphates, NH compounds**) are also clearly identified: data points corresponding to specific Raman spectra cluster together with reference spectra in the spaces defined by the principal components.

CONCLUSIONS AND FUTURE PERSPECTIVE

- PCA allows to identify **clusters of Raman spectra** related to tailpipe particulate emitted by different vehicle types, fuels and injection technologies.
- Raman spectra show the predominant presence of **black carbon** (defective graphite) across samples, confirming its status as the main component of vehicle particulate emissions.
- **Carbon nanostructures** (MWCNT-like) are detected in **raw tailpipe** samples, prior to CVS dilution.
- **Non-carbonaceous compounds**, such as iron oxides, nitrogen compounds and sulphate compounds, were detected less frequently but highlight the diversity of chemical species present in exhaust particulates.

➢ **Additional characterization techniques** will be applied to confirm the present findings: TEM and SEM/EDX (Scanning Electron Microscope coupled with Energy-Dispersive X-ray spectroscopy).
➢ **Deeper investigation** to understand how the current **CVS dilution** system may hinder the collection of MWCNT-like structures (systematically observed in **raw tailpipe particulate** samples).
➢ The same experimental approach will be applied to **non-exhaust vehicle emissions** (tires, brakes).

EU Science Hub
joint-research-centre.ec.europa.eu

Contacts:
christian.ferrarese@ec.europa.eu
dario.manara@ec.europa.eu
sara.valentini@ec.europa.eu
giorgio.martini@ec.europa.eu

Joint Research Centre

References

[1] EC, Commission Regulation (EU) 2017/1151 (2017)
[2] EC, Commission Regulation (EU) 2018/858 (2018)
[3] Jung et al. (2013), *Journal of the Air & Waste Management Association* 63(10), 1199–1204
[4] Amanatidis et al. (2014), *Environmental Science & Technology*, 48(19), 11527–11534