Raman Spectroscopy and Principal Component Analysis on fine and ultrafine particles emitted from modern vehicles.

Christian Ferrarese[1,2], Sara Valentini[2], Dora Mehn[2], Natalia E. Fonseca González[1], Dario Manara[2]

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

[2] European Commission, Joint Research Centre (JRC), Via Enrico Fermi 2749, Ispra, Italy
christian.ferrarese@ec.europa.eu

The release of particulate matter from vehicles equipped with internal combustion engines constitutes a critical concern associated with air pollution, contributing to the emergence of respiratory diseases, including lung cancers. This research focuses on advancing the accuracy and efficiency of physico-chemical and morphological characterization of particulate samples collected from the exhaust of vehicles.
The present approach entails a comprehensive examination of the morphology and molecular composition of vehicle exhaust particles, employing a combination of optical microscopy and Raman spectroscopy. Particulate samples were collected following the guidelines outlined in the European Commission Regulation 1151 (2017) [1] during driving tests performed on vehicles in chassis dyno laboratories. These tests were conducted on various modern light-duty vehicles, encompassing diesel, port fuel injection gasoline (PFI), and direct injection gasoline (GDI) models, under standardized type-approval conditions. Additionally, various particulate samples were collected and sistematically investigated during tests performed with different driving styles (simulating high congested traffic conditions, rural or highway driving), ambient temperatures, and altitudes [2]. The study also encompasses the collection of particulate samples from heavy-duty diesel vehicles, contributing to an extensive database of Raman spectra. The impact of these diverse variables on the nature of emitted particulate matter at both micrometric and sub-micrometric scales was thoroughly investigated through Principal Component Analysis (PCA) applied to a database of more than 150 spectra (Figure 1). This analytical technique enables the rapid identification of clusters of spectra with similar characteristics, providing valuable insights into the complexities of samples of particulate emitted under different conditions. Moreover, the current analysis revealed distinctive spectra in certain diesel vehicle samples, indicating the presence of unique particles characterized by carbon nanotubes, sulphates, and metal oxides. This comprehensive investigation not only enhances our understanding of the complex factors influencing the nature of particulate emissions. It also underscores the emission of particular type of particles, which can be associated with potential health risks.

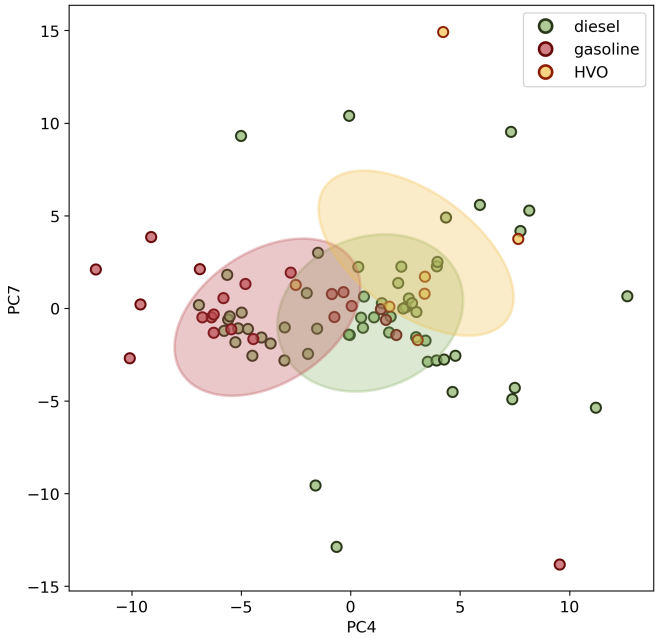

Figure 1: Example clusters identified in the Principal Component Analysis performed in this work on a broad database of Raman spectra measured on exhaust particulate emitted by Diesel, gasoline and hydrotreated vegetable oil (HVO) fuel.

[1] EC, Regulation (EU) No 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, Off. J. Eur. Union. OJ L 175 (2017) 1–643. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32017R1151

[2] C. Gruening, P. Bonnel, M. Clairotte et al., European market surveillance of motor vehicles Results of the 2022 European Commission vehicle emissions testing programme, Publications Office of the European Union, **2023**, https://data.europa.eu/doi/10.2760/452119