ECAS 2020

The 3rd International Electronic Conference on Atmospheric Sciences

16–30 NOVEMBER 2020 | ONLINE

Spectrochemical analytical characterisation of particulate matter emissions generated from in-use Diesel engine vehicles

atmosphere MDPI

Richard Viskup *, Yana Vereshchaga, Anna Theresia Stadler, Theresa Roland, Christoph Wolf, Agnes Weth and Werner Baumgartner

*emails: Viskup@gmail.com or Richard.Viskup@jku.at (R.V.)

Johannes Kepler University

Institute of Biomedical Mechatronics

Linz, Austria

JKU

Outline of the presentation

- **Motivation**
- **Introduction to**
  - Tailpipe exhaust emissions from Diesel engine vehicles
  - Solid particles - Diesel Particulate Matter (DPM) and soot
  - Laser Induced Breakdown Spectroscopy LIBS analytical technique
- **Experimental procedure**
  - LIBS setup
  - Diesel Particulate Matter collection and sample preparation
- **Experimental results**
  - Major chemical elements of Diesel Particulate Matter
  - Minor chemical elements of Diesel Particulate Matter
  - Trace chemical elements of Diesel Particulate Matter
- **Conclusion**

Motivation

- The pollutant emissions from vehicles are forming major sources of metallic nanoparticles into the environment and surrounding atmosphere
- Most of these emissions are from Diesel engine vehicles - passengers or heavy-duty truck engines
- For human health it is very important to breathe clean, non-polluted air; not only for lungs and our cardiovascular system, but also for the brain and central nervous system
- Air quality and its real situation immediately reflects on current quality of live in the cities, city-suburbs, and industrial or rural areas
- These influence a number of inhalant nanoparticles within the particulate matter PM in air, and form existing air pollution of our "modern" civilisation
- Nowadays, PM and metallic nanoparticles are the key sources of many diseases and illnesses or deaths
- After long term exposure to Particulate Matter the accumulation of nanoparticles in our body can cause the pulmonary disease, lung infection, pneumonia, asthma, cardiovascular diseases as well as neurological and mental diseases.
- Therefore, it should be among our highest priorities to rigorously explore and understand the chemical composition of particulate matter
- The knowledge of this information can help to find new techniques to precisely measure and quantify the content of different chemical elements adsorbed inside the small PM and hence minimise the vehicle's emissions.

Tailpipe exhaust emissions from Diesel engine vehicles

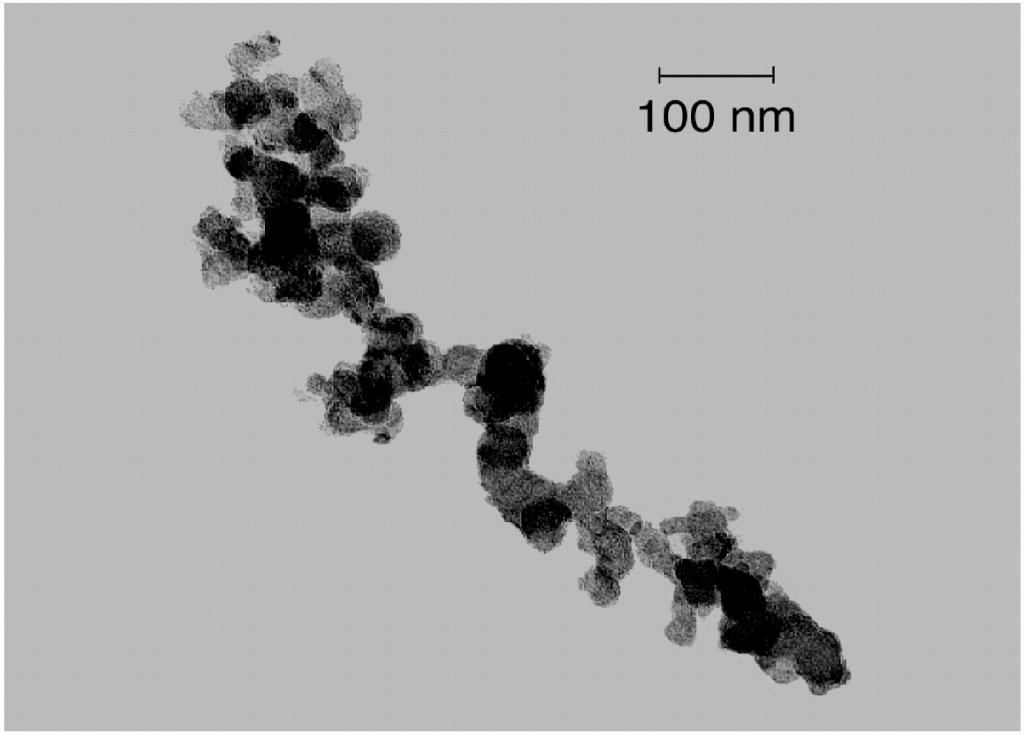
Emissions from Diesel engine vehicles exists in different forms:

- - gases, - vapour, - solid particles, - black soot, -liquid
- Gaseous compounds of Diesel emissions include
  - carbon dioxide, carbon monoxide, oxygen, nitrogen, nitrogen compounds, sulphur compounds, low molecular weight hydrocarbons, and other chemical elements and molecules adsorbed on the hydrocarbons
- Vapour phase contains
  - water vapour, larger molecular weight semivolatile organic compounds and other chemical elements dissolved in the water vapour
- Solid particles - consisting of countless elements and compounds
  - Particulates, Particulate Matter (PM), Diesel Particulate Matter (DPM), soot

Solid particles - Diesel Particulate Matter (DPM) and soot

Emissions from combustion diesel engine – black soot

- The black soot from Diesel exhaust emissions consist of Particulates, Particulate Matter (PM) or also called Diesel Particulate Matter (DPM).
- Soot - agglomerates of many primary spherical particles that differ in size, composition and solubility
- PM are composed of primary particles – spheres with diameters   5nm – 100nm or bigger
- PM consists of carbon nanoparticles and other chemical elements nanoparticles adsorbed on a carbon surface like metallic nanoparticles and other chemical elements.



TEM micrograph of soot particle from diesel engine picture from Ref. [1]

LIBS as analytical tool for spectrochemical Diesel Particulate Matter analyses

- In order to minimise exhaust emissions from combustion vehicles and unwanted pollutants into the atmosphere it is important to identify all potential sources of these emissions
- One of the source are particulates, Diesel Particulate Matter from Diesel engine passenger vehicles
- Therefore it is necessary to explore the composition of Diesel Particulate Matter – especially - chemical elements contained in the exhaust emissions generated from the in-use Diesel engine passenger vehicles
- Here we apply sensitive, high resolution spectroscopic technique – Laser Induced Breakdown Spectroscopy (LIBS), also called plasma spectroscopy (LIPS) for accurate spectrochemical analyses of DPM exhaust emissions
- Laser-induced plasma spectroscopy is a versatile and sensitive non destructive contact less optical technique use for compositional analysis of many different classes of materials: solids, liquid, gaseous, powder or nanoparticles

Laser Induced Breakdown Spectroscopy

- **LIBS / LIPS technique**
  - has wide potential for different applications in various fields: environmental, industrial, geological, geochemical, planetary / space exploration, in art and cultural heritage, as well as for medical, biological and biomedical applications.

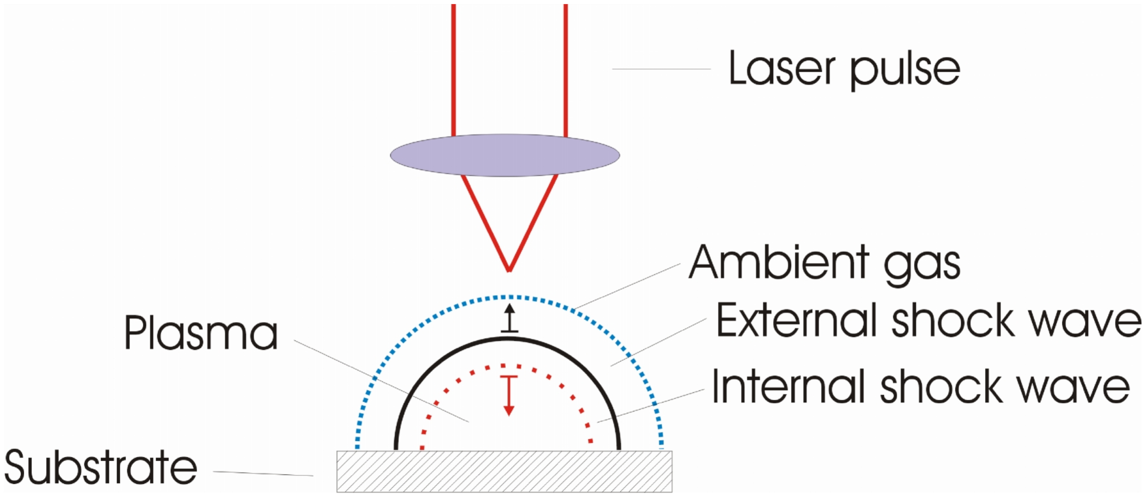
For further details see Ref. [2, 3]

- **A few reasons why LIBS / LIPS is very powerful method for material analyses:**
  - fast and accurate laser technique in ppm level
  - ability to perform compositional analysis from single or multiple laser shot/s
  - virtually no /or very little sample preparation
  - instant results
  - for major and/or minor chemical elements detection
  - in-situ technique
  - possibility to be use for real time monitoring
  - for 2D or 3D mapping
  - for sample / material classification

For further details see Ref. [4]

Plasma formation

- High fluence laser pulse leads to ablation of the target material
- This high power and focused laser radiation cause ionization of the matter and produce a plasma
- Plasma consists of clusters, molecules, atoms, ions and electrons, etc.



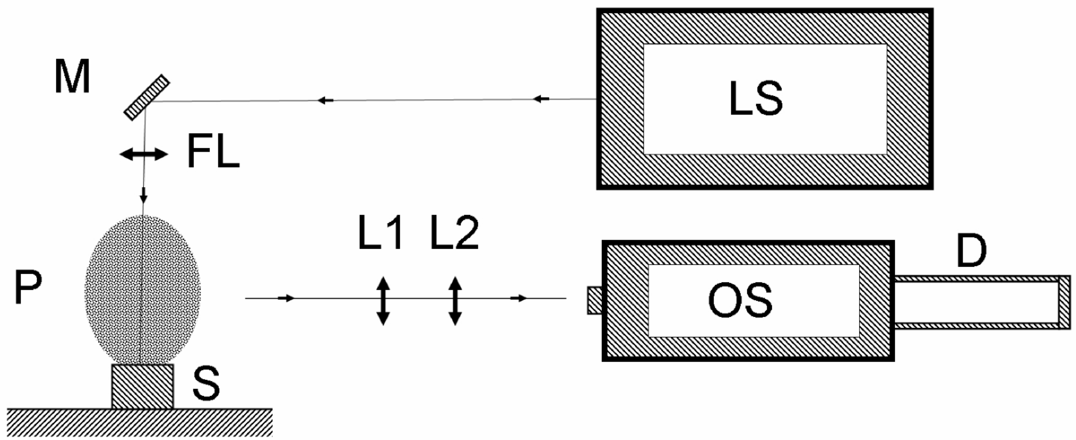
- Photography of ns laser plasma from Nd:YAG laser in air atmosphere.

For further details see Ref. [5]

LIBS experimental setup

- Schema of experimental Laser Induced Breakdown Spectroscopy (LIBS) set-up for analyses of Diesel Particulate Matter

Nd:YAG Laser
λ=1064 nm
E ~ 300mJ
High resolution spectrograph
ICCD Gate time: 2 μs
Spectral window 190nm – 800 nm



Schema of laser-induced breakdown spectroscopy (LIBS):

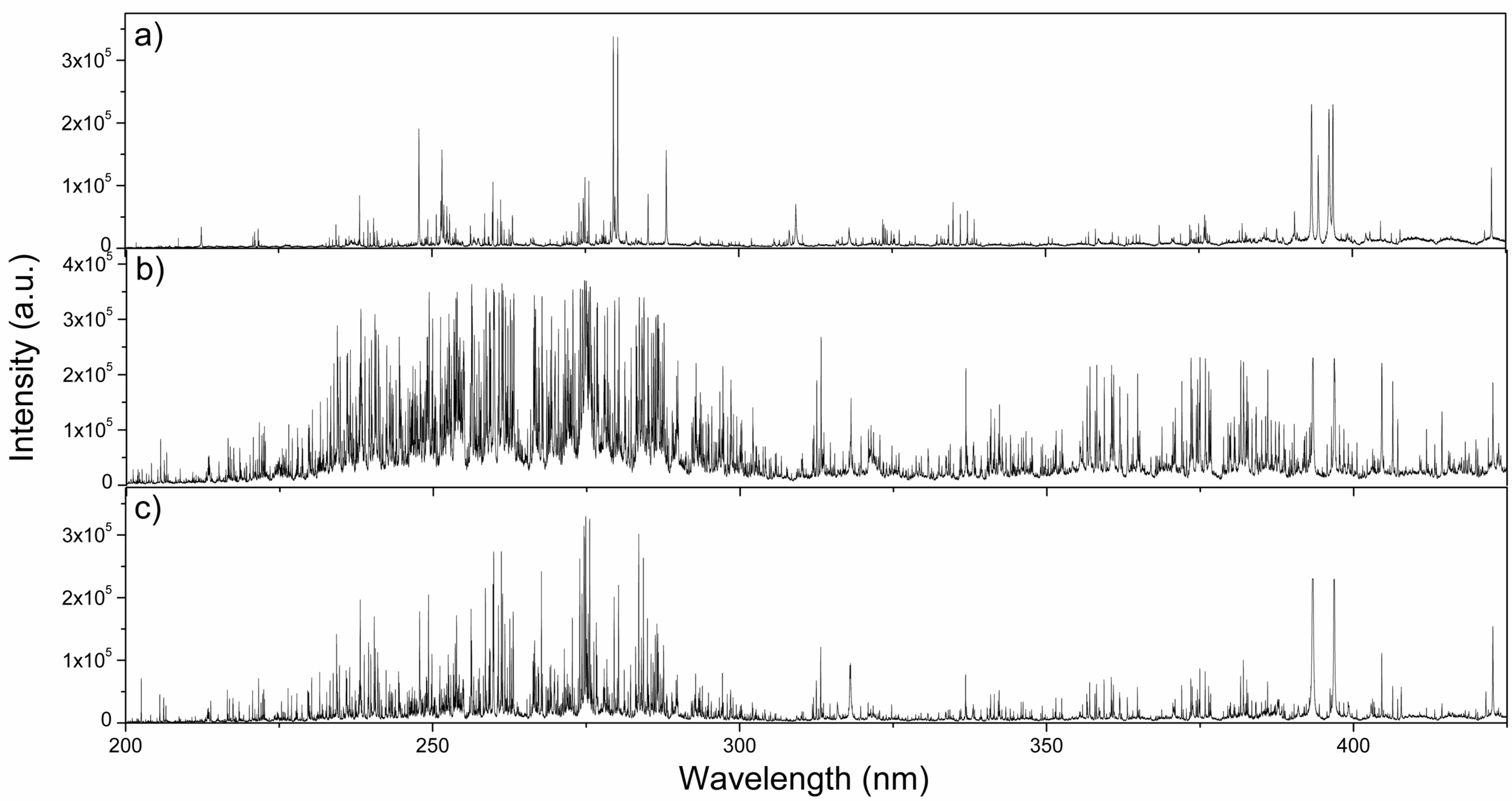
LS—Laser Source (Nd:YAG laser, Yasmin, Quantel, France), M—Mirror, P—Plasma, S—Sample, FL—Focusing Lens, L1 and L2—Optical Telescope, OS—Optical Spectrometer (Aryelle Butterfly, Echelle spectrograph, LTB Berlin, Germany), D— Intensified Charge Coupled Device (ICCD) Detector, PI-Max 4, Princeton Instruments, USA.

Diesel Particulate Matter collection

- Diesel Particulate Matter were collected from different Diesel engine passenger vehicles
- Selection of vehicles were performed randomly and no company has been preferred
- DPM collection from major brand car producers in Europe
- 67 different DPM samples analysed by LIBS
- Position of collection DPM:
  - tailpipe
  - at the end of the exhaust manifold
  - or after the Diesel Particulate Filter (DPF) if applied
- Engine: no test bench, no test engine vehicle
- In-use Diesel engine passenger vehicles
- Samples of particulate matter – PM deposits extracted from tail pipe were mechanically pressed into the flat disc-like shape pellets with diameter - 6 mm

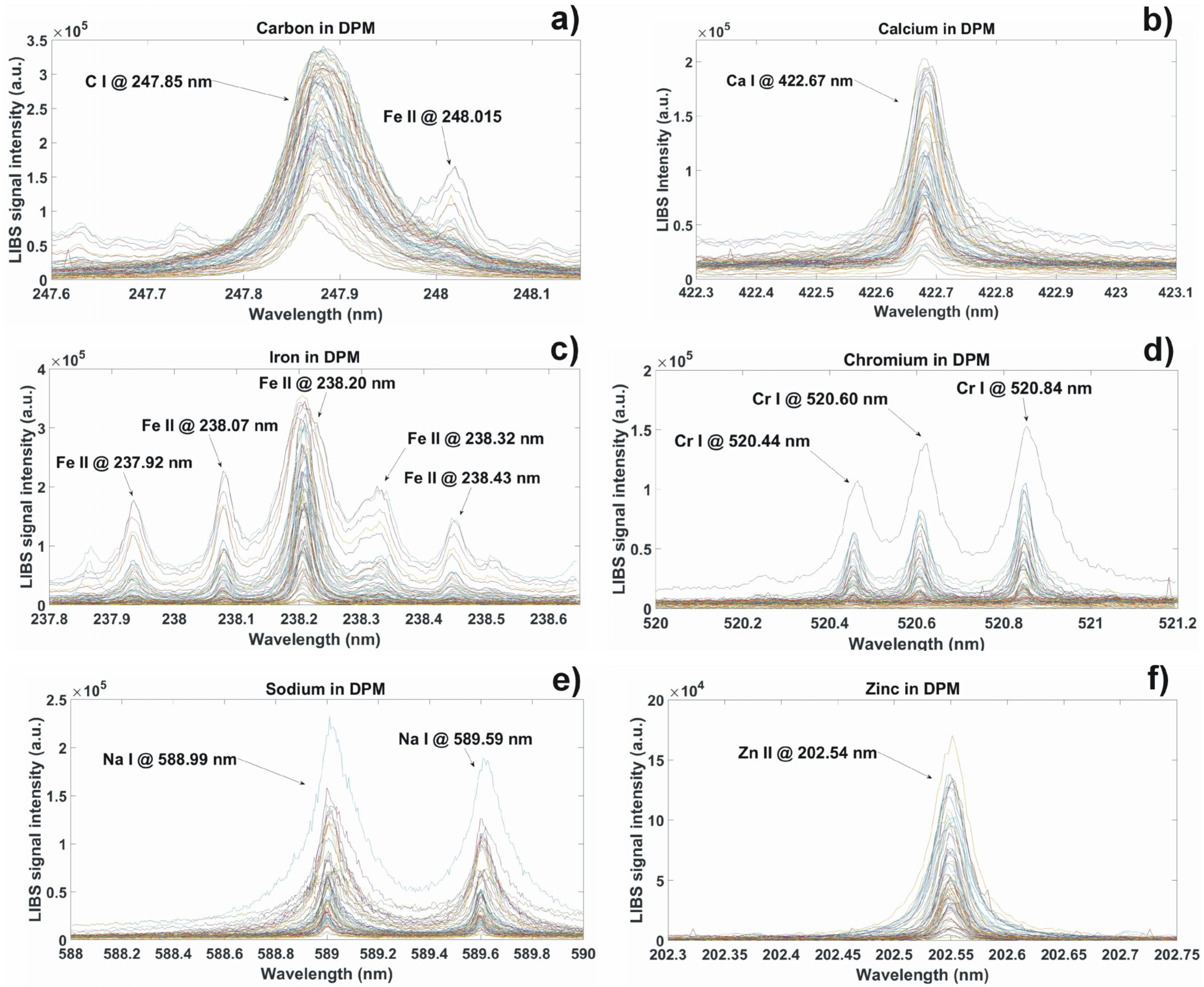
Major chemical elements of Diesel Particulate Matter

- Laser Induced Breakdown Spectroscopy signal measured from three different Diesel Particulate Matter (DPM) samples.
- Intense spectral lines are from major chemical elements:
  - Spectrum **a)** Ca, Mg, Zn
  - Spectrum **b)** Ca, Cr, Fe, H, Mg, Na
  - Spectrum **c)** Al, C, Ca, Cr, Mg, O
- These chemical elements are forming major concentrations of DPM. For further reference see Ref. [6,7]



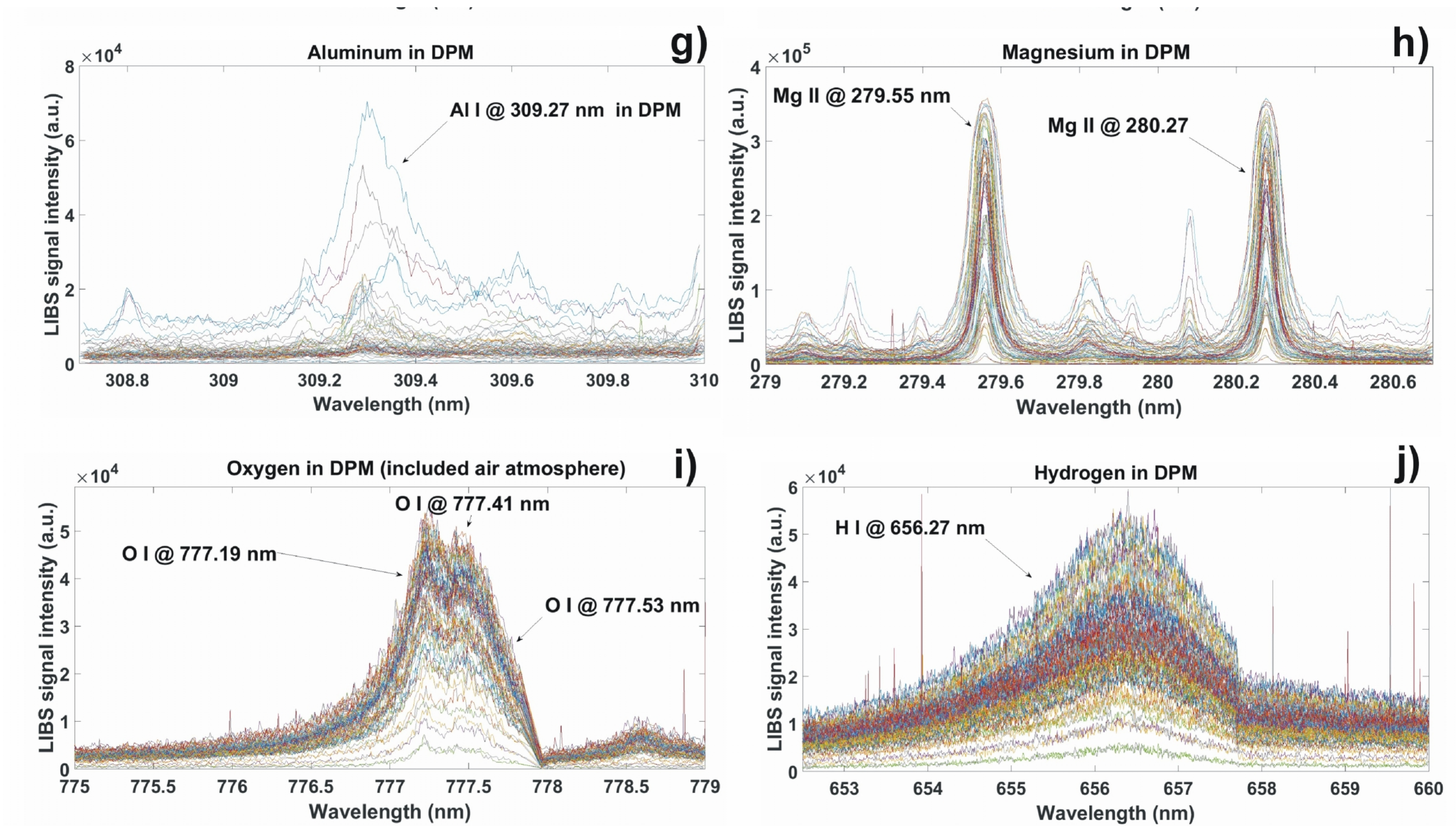
Major chemical elements of Diesel Particulate Matter I

- High resolution LIBS spectra from 67 samples of Diesel Particulate Matter extracted from in-use Diesel engine passenger vehicles.
- Optical emission is from **major chemical elements**:
  - (a) Carbon, (b) Calcium, (c) Iron, (d) Chromium, (e) Sodium, (f) Zinc



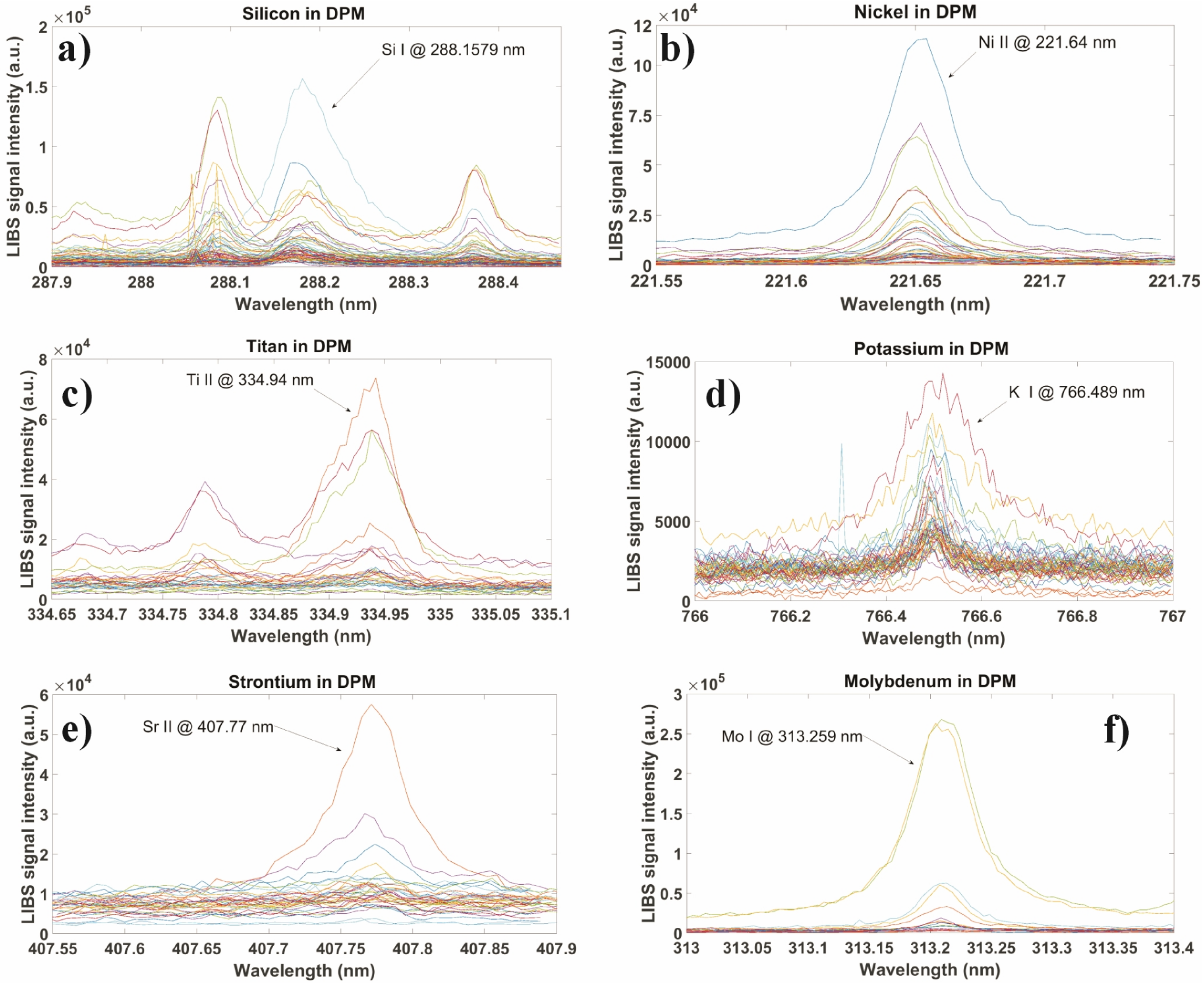
Major chemical elements of Diesel Particulate Matter II

- High resolution LIBS spectra from 67 samples of Diesel Particulate Matter extracted from in-use Diesel engine passenger vehicles.
- Optical emission is from **major chemical elements**:
  - (g) Aluminum, (h) Magnesium, (i) Oxygen, (j) Hydrogen



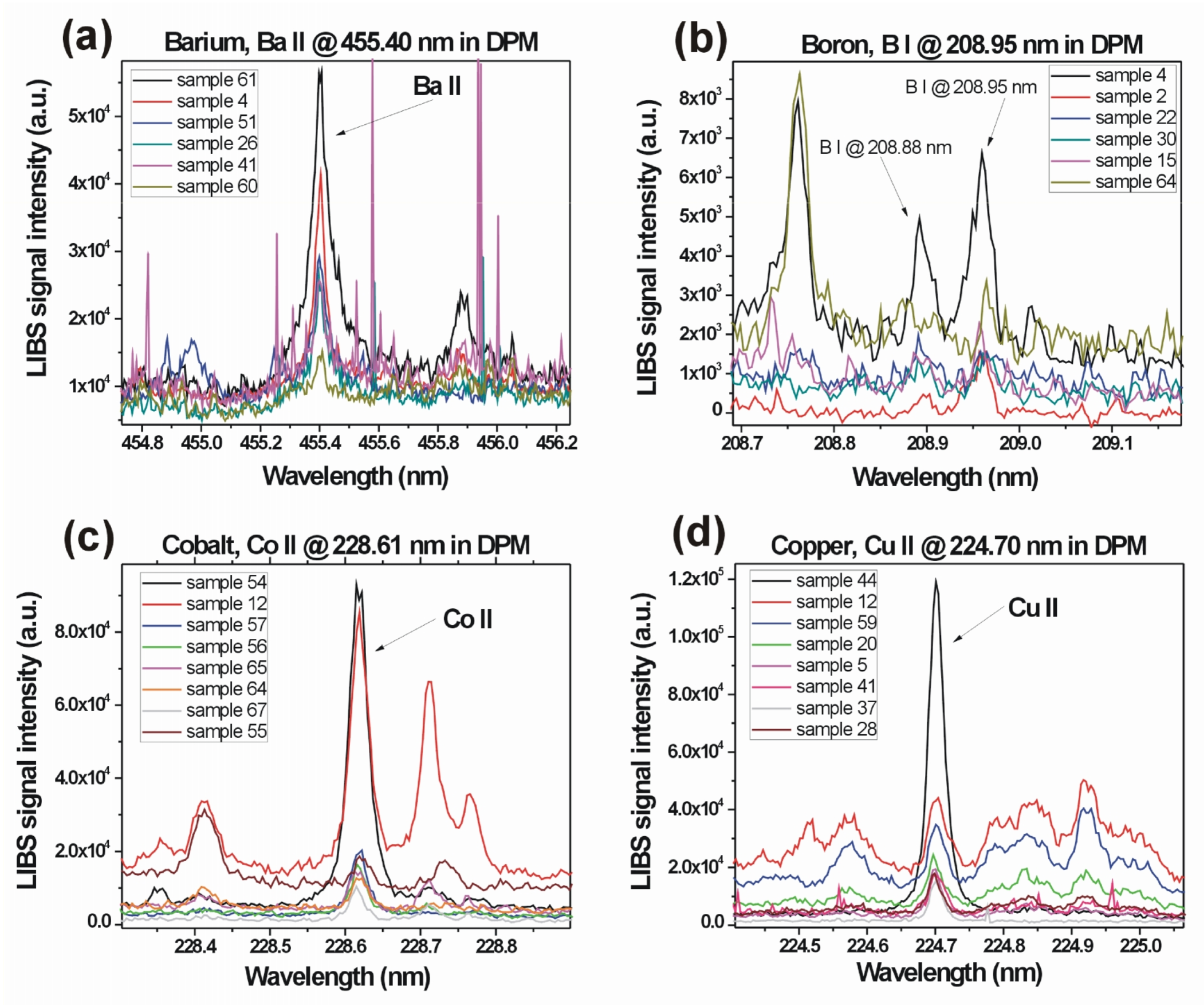
Minor chemical elements of DPM

- High resolution LIBS spectra from 67 samples of Diesel Particulate Matter extracted from in-use Diesel engine passenger vehicles.
- LIBS optical emission spectra from **minor chemical elements**:
  - a) Silicon, b) Nickel, c) Titan, d) Potassium, e) Strontium, f) Molybdenum



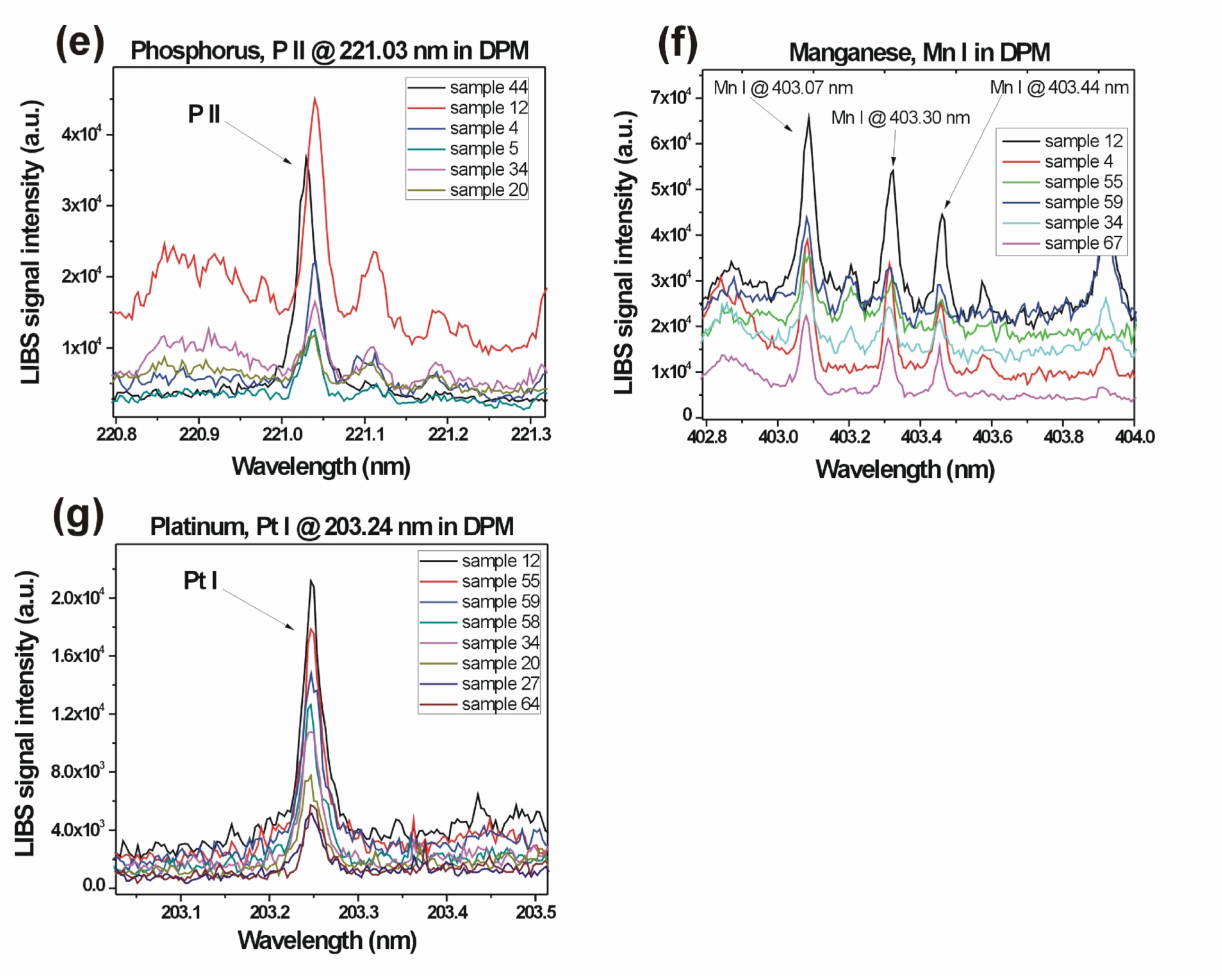
Trace chemical elements of Diesel Particulate Matter I

- High resolution LIBS spectra from 67 samples of Diesel Particulate Matter extracted from in-use Diesel engine passenger vehicles.
- Optical emission spectra from **trace elements**:
  - (a) Barium, (b) Boron, (c) Cobalt, (d) Copper



Trace chemical elements of Diesel Particulate Matter II

- High resolution LIBS spectra from 67 samples of Diesel Particulate Matter extracted from in-use Diesel engine passenger vehicles.
- Optical emission spectra from **trace elements**:
  - (e) Phosphorus, (f) Manganese and (g) Platinum



Conclusion

- In presented study we spectrochemicaly characterise particulate matter emissions from in-use Diesel engine passenger vehicles
- Diesel particulate matter (DPM) were collected from more than 70 different in-use Diesel engine passenger vehicles.
- We used random selections of in-use Diesel engine passenger vehicles from daily life environment .
- DPM from in-use vehicles does not consists of only carbon / carbon black particles. DPM is composed of major, minor and trace chemical elements.
- The major compound of DPM is not strictly Carbon element, but also other adsorbed nanoparticles such as Iron, Chromium, Aluminium, Zinc, Magnesium, Calcium, Sodium, Oxygen and Hydrogen.
- Minor chemical elements of DPM analysed by LIBS are: Silicon, Nickel, Titan, Potassium, Strontium and Molybdenum.
- Additionally in DPM are adsorbed atomic trace elements: Barium, Boron, Cobalt, Copper, Phosphorus, Manganese and Platinum.
- All these chemical elements are forming significant atomic composition of real particulate matter from in-use Diesel engine passenger vehicles.
- The chemical composition of individual DPM matrices varies considerably. This is due to the different origins of each particulate matter sample – different vehicle.
- The DPM composition can altered due to complex engine processes as well as type of vehicle, age, and additional input parameters as are: type of Diesel fuel, fuel additives, composition of the intake air, quality of combustion process, type and performance of the Diesel engine, lubrication oil, erosion on the piston rings or cylinder liner. Other parts that influence the matrix composition are applied pre-treatment and aftertreatment devices, like Diesel particle filters (DPF) or catalysts like Selective Catalytic Reduction devices etc.
- All these information will be helpful for developing of LIBS method as accurate in-situ technique for on-line elemental composition analyses of particulate matter emissions from vehicles and hence to be able to minimise the pollutant emissions from in-use Diesel engine driven vehicles.

References

[1] Schraml S., Anwendung der laserinduzierten Glühtechnik zur Rußdiagnostik dieselmotorischer Verbrennungsprozesse, BEV, Schriftenreihe Heft 1.6, Erlangen, 2001.

[2] Noll, R. *Laser-Induced Breakdown Spectroscopy, Fundamentals and Applications*; Springer-Verlag: Berlin, Germany, 2012.

[3] Miziolek, A.W.; Palleschi, V.; Schechter, I. *Laser-Induced Breakdown Spectroscopy (LIBS): Fundamentals and Application*; Cambridge University Press: New York, NY, USA, 2006.

[4] Cremers, D.A.; Radziemski, L.J. *Handbook of Laser-Induced Breakdown Spectroscopy*; John Wiley & Sons Inc.: New Delhi, India, 2013.

[5] Viskup, R. Single and Double Laser Pulse Interaction with Solid State–Application to Plasma Spectroscopy. In *Nd YAG Laser*; Dumitras, D.C., Ed.; InTech: Rijeka, Croatia, 2012; ISBN 978-953-51-0105-5, doi:10.5772/35288.

[6] Viskup R, Wolf C, Baumgartner W, Qualitative and quantitative characterisation of major elements in particulate matter from in-use diesel engine passenger vehicles by LIBS. Energies. 2020;13:368. DOI: 10.3390/en13020368

[7] Viskup R, Wolf C, Baumgartner W, Major Chemical Elements in Soot and Particulate Matter Exhaust Emissions Generated from In-Use Diesel Engine Passenger Vehicles, Introduction to Diesel Emissions, Richard Viskup, IntechOpen, DOI: 10.5772/intechopen.90452.

Acknowledgement

- to the Austrian Science Fund - FWF for providing financial support under the project number [FWF P27967].

JOHANNES KEPLER UNIVERSITÄT LINZ

Der Wissenschaftsfonds.

Thank you for your attention