ASEC 2020
1st International Electronic Conference on Applied Sciences
10–30 NOVEMBER 2020 | ONLINE

Qualitative and quantitative characterisation of minor chemical elements in Diesel Particulate Matter by Laser Induced Breakdown Spectroscopy

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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**
  - Main chemical elements of Diesel Particulate Matter
  - Minor chemical elements of Diesel Particulate Matter
  - Quantitative determination of minor chemical elements in Diesel Particulate Matter
- **Conclusion**

Motivation

- Diesel engine emissions and Diesel vehicles emission monitoring are hot topics nowadays
- Quality of air and its real situation immediately reflects on current quality of live in the cities, city-suburbs, and industrial or rural areas
- Thus influence the number of inhalant nanoparticles within the particulate matter in air, and form the current air pollution of our "modern" civilisation
- To inhale non-polluted and clean air is extremely important for our human health – not only for lungs and cardiovascular system, but also for the brain and central nervous system
- Nowadays, PM and metallic nanoparticles are the key sources of many diseases and illnesses or deaths
- 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

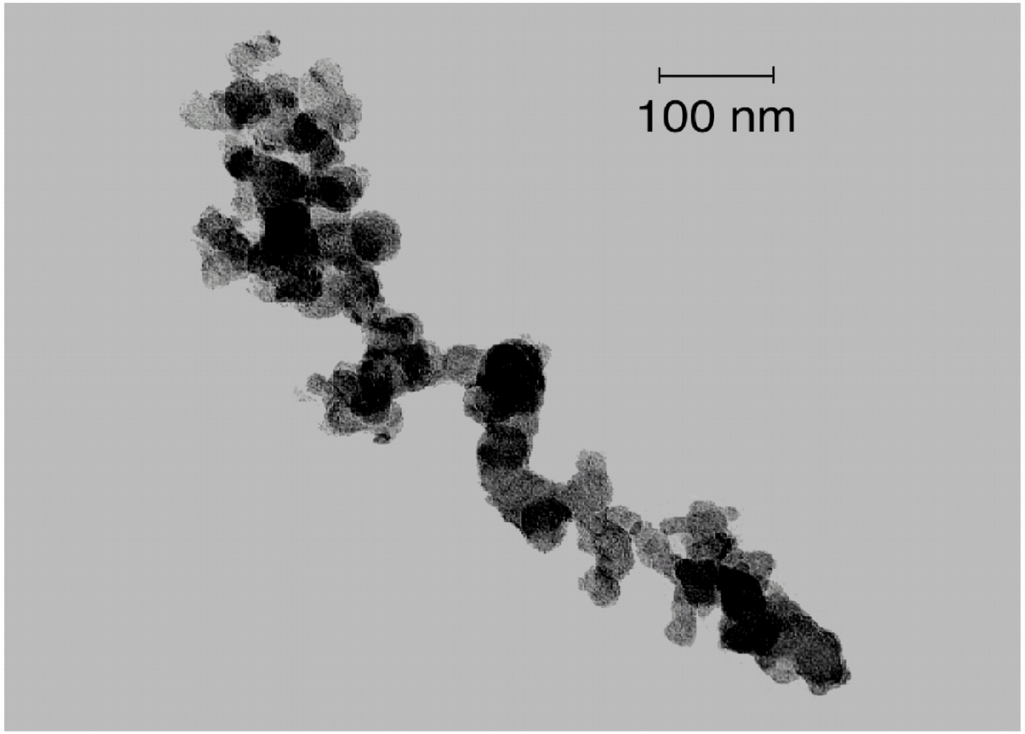
Emissions from Diesel engine vehicles exists in different forms:

- - 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.

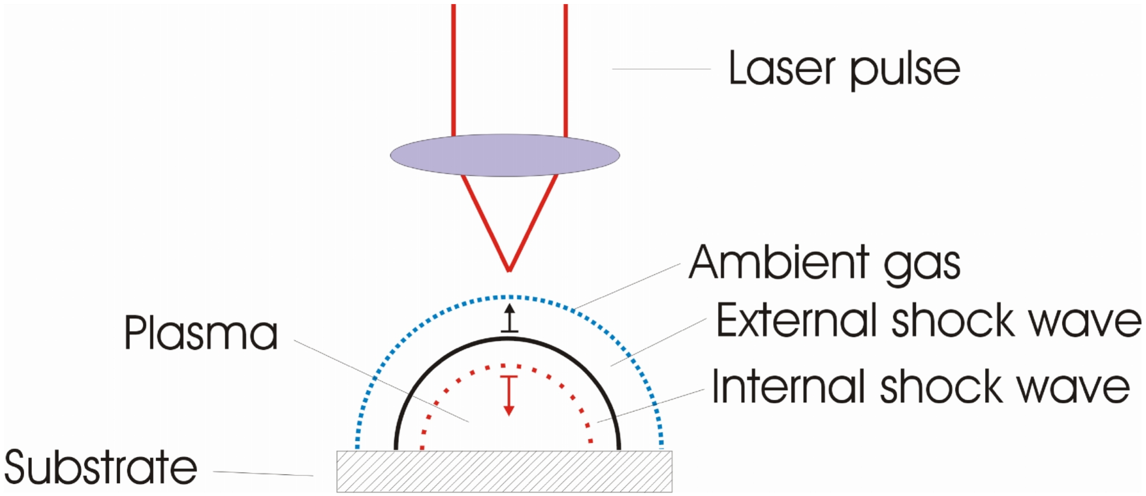
For further details see Ref. [2, 3]

- **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.



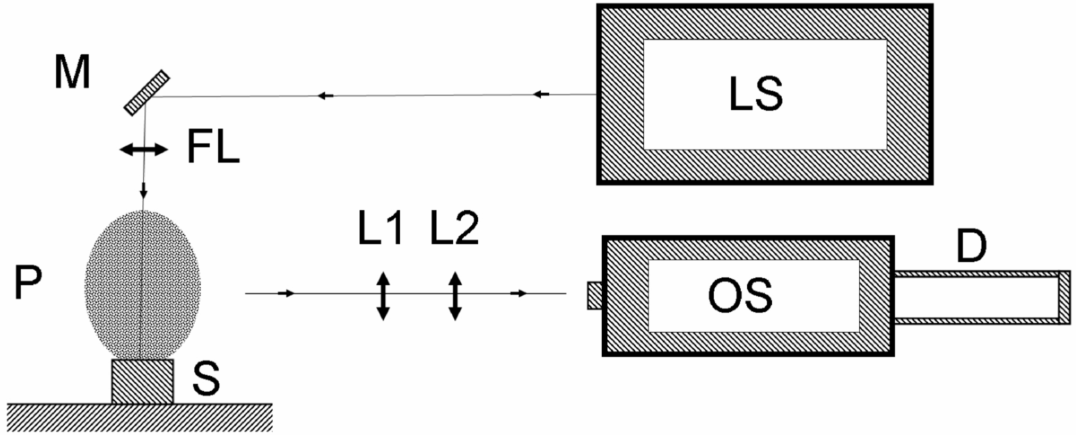
- Photography of ns laser plasma from Nd:YAG laser in air atmosphere.

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):

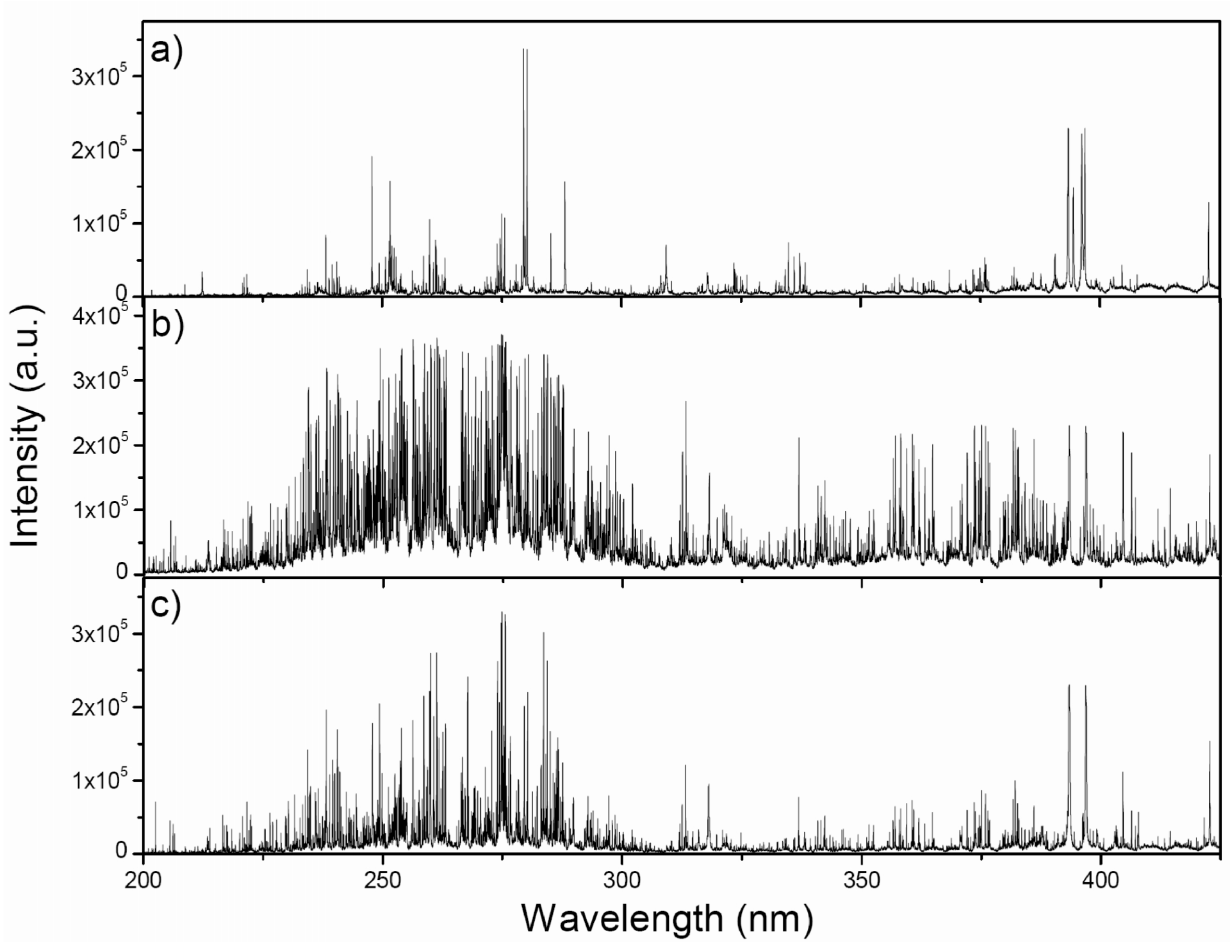
LS—Laser Source (Nd:YAG laser, Yasmin, Quantel, France), M—Mirror, P—Plasma, S—Sample, FL—Focusing Lens, L1 and L2—Optical Telescope, OS—Optical Spectrometer (Aryelle Butterfly, Echelle spectrograph, LTB Berlin, Germany), D— Intensified Charge Coupled Device (ICCD) Detector, PI-Max 4, Princeton Instruments,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

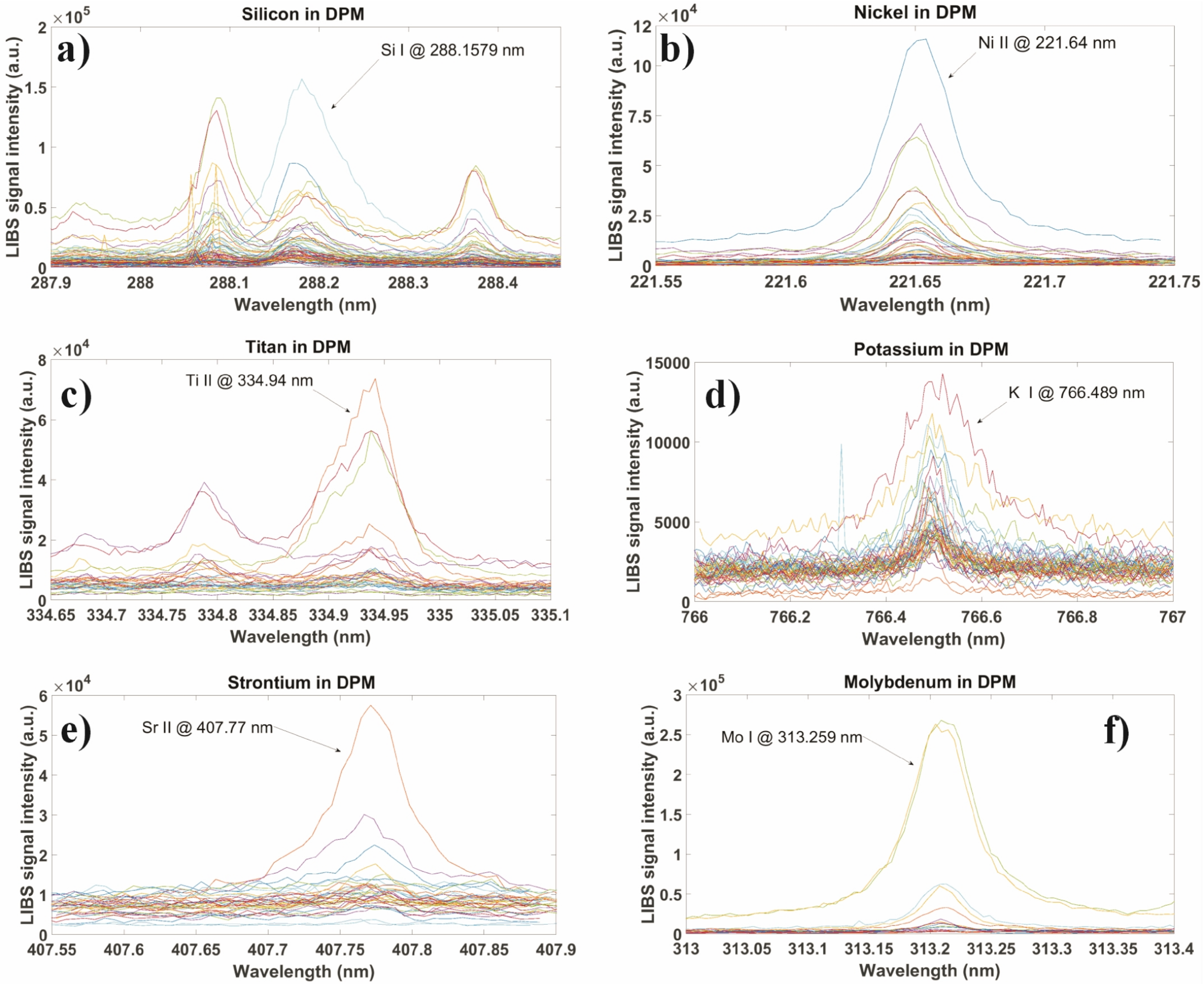
Main chemical elements of Diesel Particulate Matter

- In the figure are shown three different LIBS spectra from DPM - samples collected from in-use Diesel engine passenger vehicles
- Optical emission spectra measured by LIBS technique
- LIBS data reveal high content of:
  - a) Carbon, b) Iron, c) Magnesium. d) Aluminium, e) Chromium, f) Zinc, g) Sodium and h) Calcium elements
- These chemical elements form the major concentrations of DPM for further details see Ref. [6,7]



Minor chemical elements of DPM

- Minor chemical elements contained in the Diesel Particulate Matter generated from in-use Diesel engine passenger vehicles and analysed by high resolution Laser Induced Breakdown Spectroscopy technique



- Measured optical emission spectra are from:
  - a) Silicon, b) Nickel, c) Titan, d) Potassium, e) Strontium, f) Molybdenum

Detected minor elements in Diesel Particulate Matter samples

Silicon (Si), Nickel (Ni), Titan (Ti), Potassium (K), Strontium (Sr), Molybdenum (Mo)

Analyte	Spectral line	Wavelength (nm)	Detected in / total number of samples
Si	Si I	288.15	63 / 67
Ni	Ni II	221.64	43 / 67
Ti	Ti II	334.94	32 / 67
K	K I	766.48	50 / 67
Sr	Sr II	407.77	35 / 67
Mo	Mo I	313.25	17 / 67

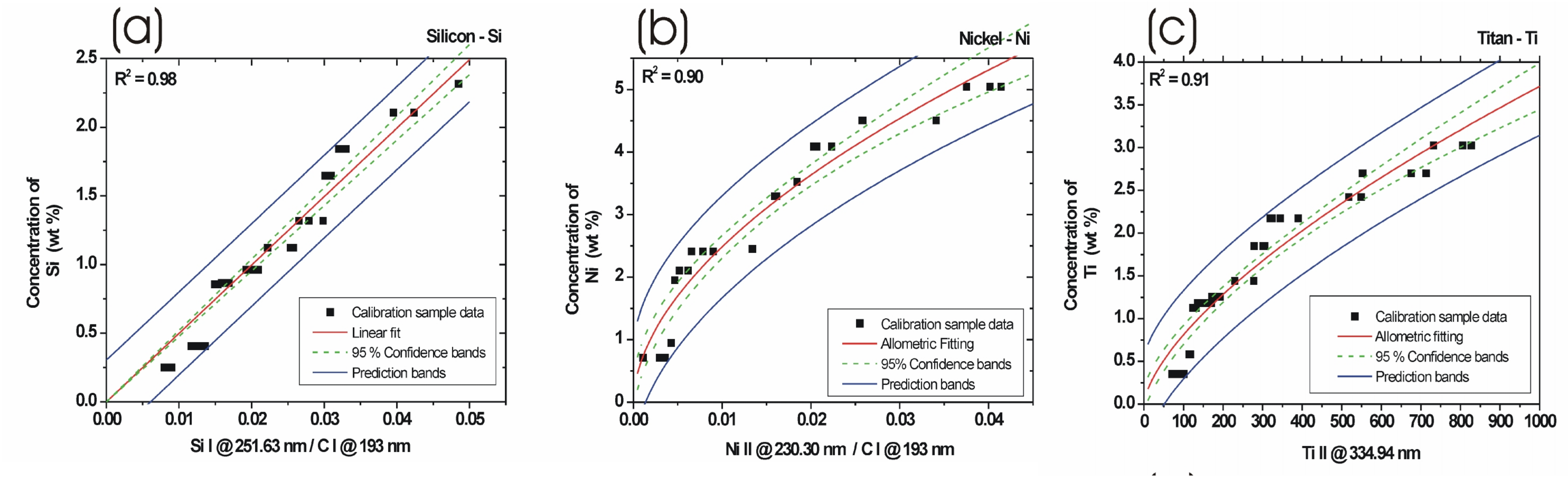
- Spectral lines and wavelengths - spectral atomic and ionic lines employed for LIBS analytical measurements
- Number of samples with detected chemical element
- The spectral lines data are from the National Institute of Standards and Technology (NIST) atomic spectra database

Calibration procedure

- Preparing internal laboratory calibration standards
- Laboratory standards were prepared with different concentrations of major and minor chemical elements similar to DPM
- Qualitative LIBS measurements from minor elements in DPM used
- Previous results from qualitative and quantitative LIBS measurements from major chemical elements and concentrations in DPM were also used
- Internal standards were made from pure certified elements
- Major group of chemical elements in calibration samples are due to the high intensity and signal strength in DPM measured by LIBS technique from:
  - Carbon, Iron, Zinc, Calcium and Magnesium
- Minor elements of laboratory prepared calibration samples are due to the lower signal measured by LIBS in DPM from:
  - Molybdenum, Nickel, Potassium, Silicon, Strontium and Titan
- Laboratory calibration standards were produced as mixtures of nano-powder materials

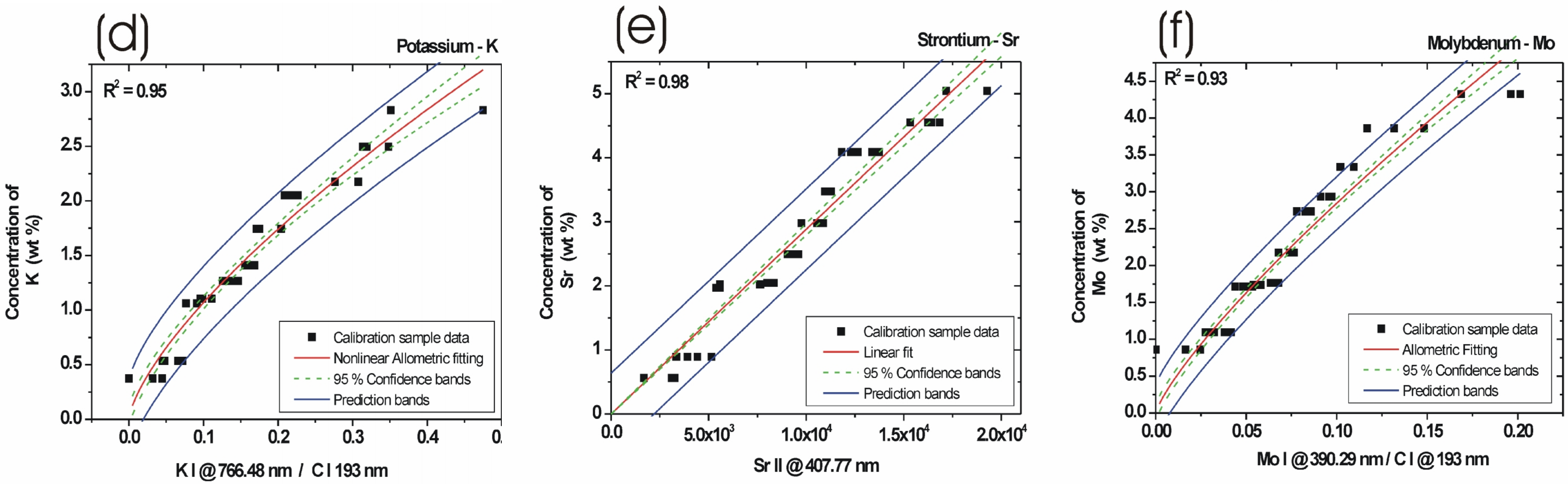
Calibration functions

- Calibration curves - red line
- regression parameter R2
- 95% confidence limits - green dashed line
- prediction bands - blue line
- Calibration functions (**a**) Silicon, (**b**) Nickel, (**c**) Titan
- LIBS data are from laboratory prepared PM calibration standards
- Concentrations of chemical elements in weight percent (wt %).



Calibration functions

- LIBS calibration functions
  - (**d**) Potassium
  - (**e**) Strontium
  - (**f**) Molybdenum



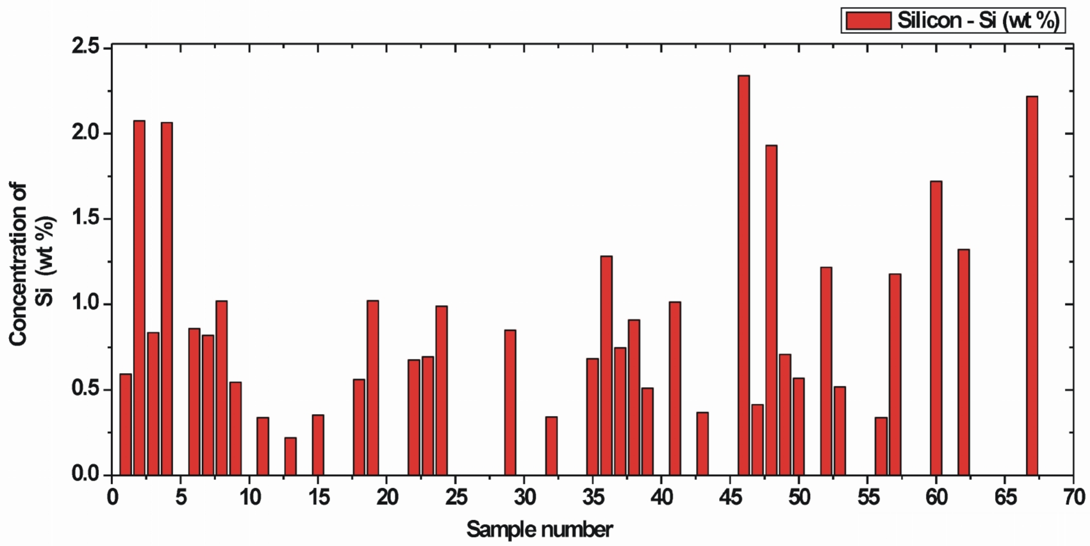
Summary of calibration procedure

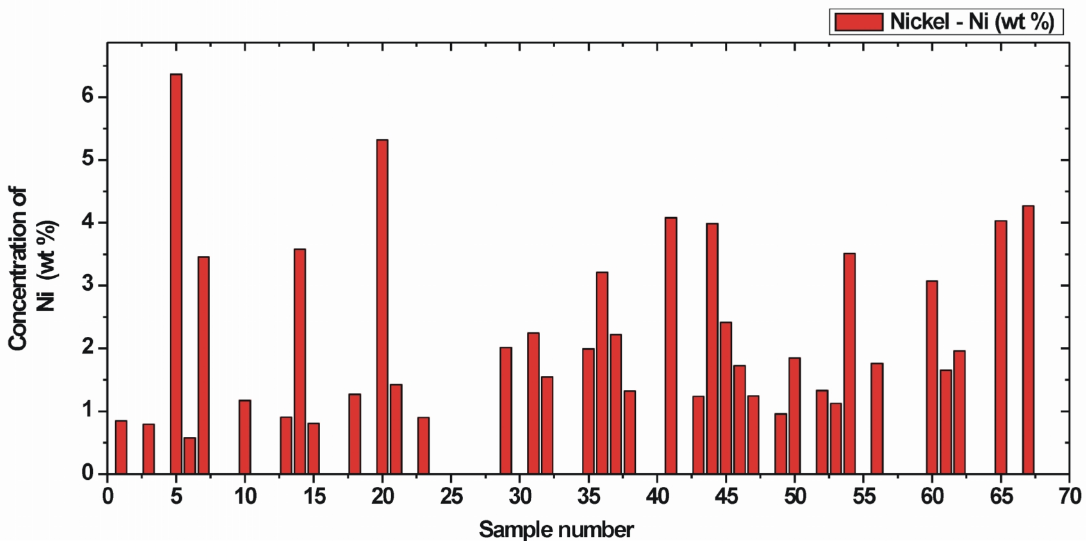
- Minor chemical elements in DPM: Si, Ni, Ti, K, Sr, Mo
- calculated regression parameter R2
- concentration interval in (wt %) valid for calibration curves
- Measured spectral lines and ratios of chemical elements used for LIBS signal processing

Calibration for analyte	Regression parameter R^2	Calibration for concentrations wt %	Optical spectral lines and integrated peak ratio for calculation
Si	0.98	0 - 3	Si I @ 251.63 nm, C I @ 193.02 nm
Ni	0.90	0 - 7	Ni II @ 230.30 nm, C I @ 193.02 nm
Ti	0.91	0 - 4	Ti II @ 334.94 nm
K	0.95	0 - 3	K I @ 766.48nm, C I @ 193.02 nm
Sr	0.98	0 - 5	Sr II @ 407.77 nm
Mo	0.93	0 - 6	Mo I @ 390.29 nm, C I @ 193.02 nm

Quantitative determination of minor chemical elements in DPM I.

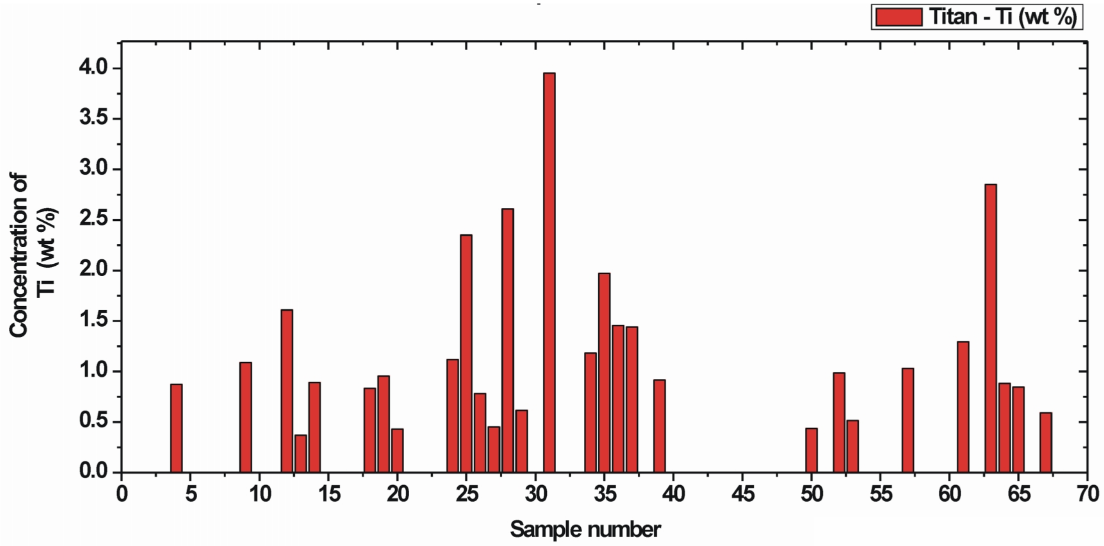
- Concentration of minor chemical elements in different DPM
- DPM collected from in – use Diesel engine passenger Vehicles
- measured by LIBS, units are in weight percent (wt %)
  - Silicon – Si
  - Nickel - Ni

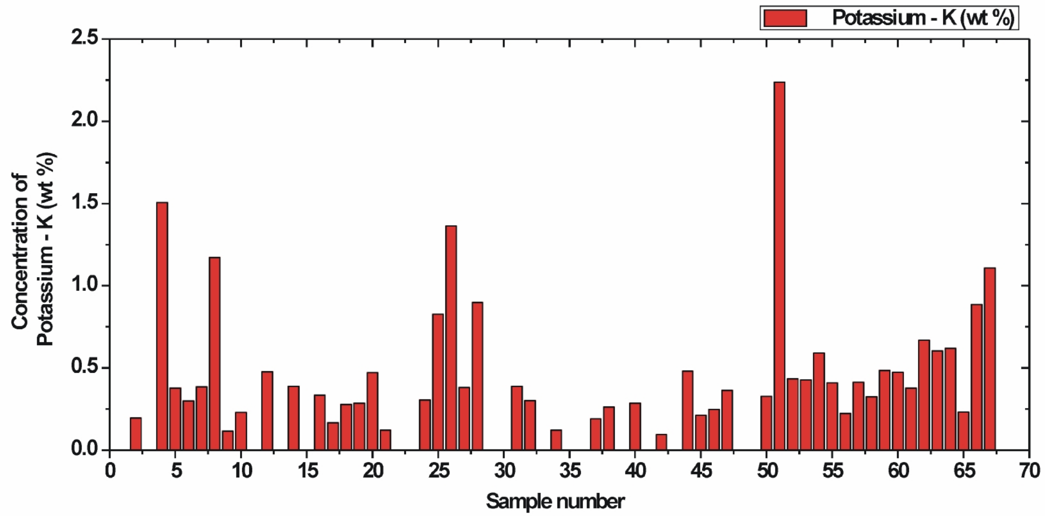




Quantitative determination of minor chemical elements in DPM II.

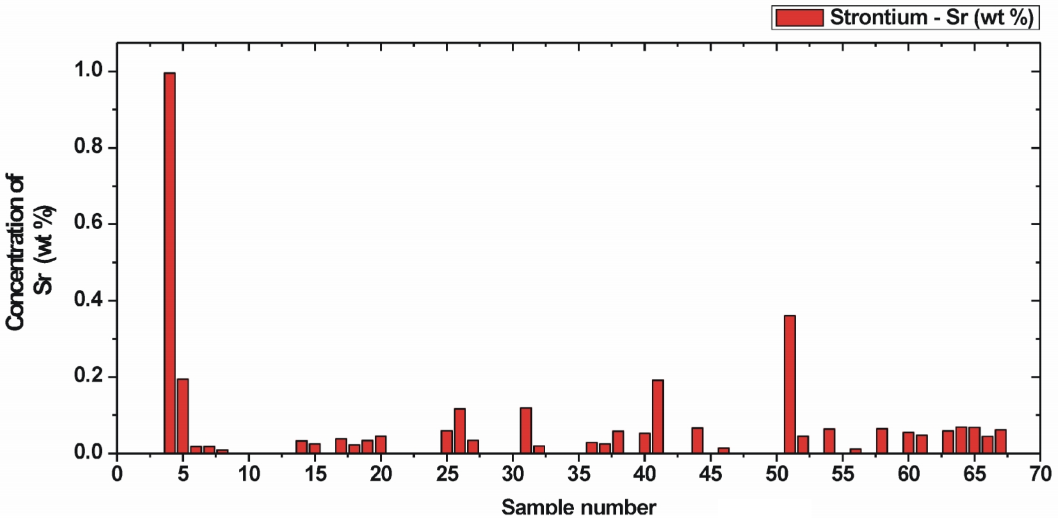
- Concentration of chemical elements in different DPM
- DPM collected from in – use Diesel engine passenger Vehicles
- measured by LIBS, units are in weight percent (wt %)
  - Titan – Ti
  - Potassium - K

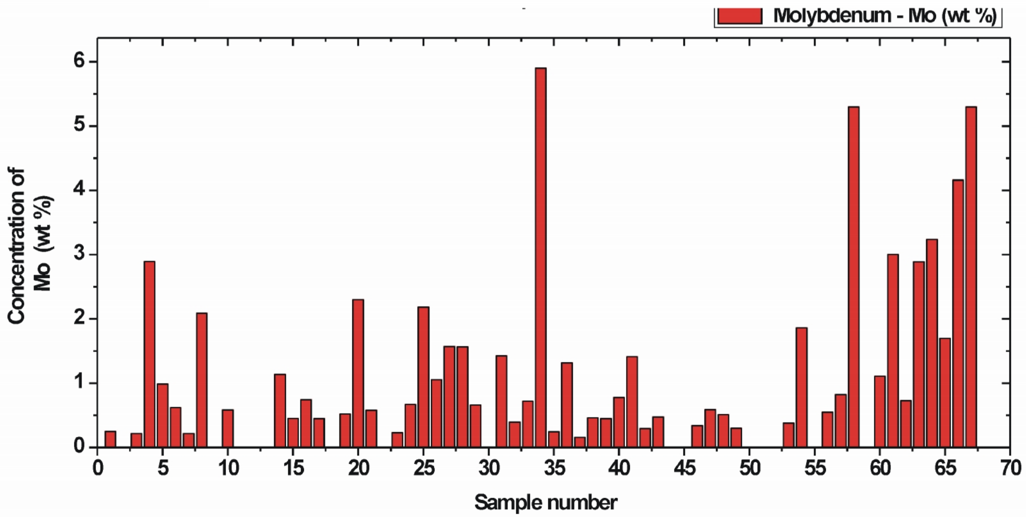




Quantitative determination of minor chemical elements in DPM III.

- Concentration of chemical elements in different DPM
- DPM collected from in – use Diesel engine passenger Vehicles
- measured by LIBS, units are in weight percent (wt %)
  - Strontium – Sr
  - Molybdenum - Mo





Concentration of chemical elements in different DPM

- **Summary Table:**
  - Concentration of chemical elements in different Diesel Particulate Matter
  - Diesel particulate matter collected from in – use Diesel engine passenger Vehicles
  - Minor chemical elements of DPM: Si, Ni, Ti, K, Sr, Mo
  - Maximum, minimum, meanvalue and median value are in weight percent (wt %) units

Analyte	Max. concentration (wt %)	Min. concentration (wt %)	Mean value (wt %)	Median value (wt %)	Number of DPM samples used for statistics
Si	2.33	0.22	0.94	0.81	37
Ni	6.36	0.57	2.22	1.76	37
Ti	3.95	0.36	1.21	0.95	29
K	2.23	0.1	0.48	0.37	50
Sr	0.99	0.01	0.09	0.04	35
Mo	5.9	0.16	1.32	0.72	52

Conclusion

- In presented research we qualitatively and quantitatively characterise the minor chemical elements in Diesel Particulate Matter by Laser Induced Breakdown Spectroscopy.
- 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 .
- Laser Induced Breakdown Spectroscopy (LIBS) measurements of 67 different DPM samples.
- DPM from in-use vehicles does not consists of only carbon (carbon black) particles. However it contains many additional major and minor chemical elements in various concentrations.
- In our previous study we apply LIBS to analysed DPM samples and determine the major elements .
- Major chemical elements of DPM are due to the high concentrations: Carbon, Iron, Magnesium, Aluminium, Chromium, Zinc, Sodium and Calcium in DPM matrices (for further details see Ref: 6, 7).
- Minor chemical elements of DPM analysed by LIBS are: Silicon, Nickel, Titan, Potassium, Strontium and Molybdenum due to the lower concentrations of these elements in DPM matrices (few %).
- 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.
- Understanding the chemical composition of Diesel particulate matter can help to better control the engine, as well as combustion process, and thus reduce unwanted emissions generated by Diesel engine powered vehicles in real driving situations, to meet future emission standards.

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Acknowledgement

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

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FWF Der Wissenschaftsfonds.

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