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

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Abstract: The pollutant emissions from vehicles are forming major sources of metallic nanoparticles into the environment and surrounding atmosphere. In this research we spectrochemicaly analyse chemical composition of Particle Matter emissions from in-use Diesel engine passenger vehicles. We have extracted Diesel Particulate Matter from the end part of the tail pipe, from more than seventy different vehicles. And in laboratory we have used the high resolution laser induced plasma spectroscopy (LIBS) spectrochemical analytical technique to sensitively analyse chemical elements in different DPM. We have found that PM is composed of major, minor and trace chemical elements. The major compound of PM is not strictly Carbon element but rather other adsorbed metallic nanoparticles such as Iron, Chromium, Magnesium, Zinc, Calcium. Beside the major elements of DPM there are also minor elements: Silicon, Nickel, Titan, Potassium, Strontium, Molybdenium and others. Additionally in DPM are adsorbed atomic trace elements like Barium, Boron, Cobalt, Copper, Phosphorus, Manganese and Platinum. All these chemical elements are forming significant atomic composition of real PM from in-use Diesel engine vehicles.

Keywords: air quality; air pollution; fine aerosol particles; ultrafine particles; black carbon; Particulate Matter; Diesel Particulate Matter; particulates; soot; carbon emissions; pollutant emissions; vehicle emissions; exhaust emissions; metallic nanoparticles; trace metals; trace elements; trace emission; epidemiology; toxicology; optical emission spectroscopy; laser induced breakdown spectroscopy; laser induced plasma spectroscopy; LIBS; LIPS

1. Introduction

The pollutant emissions from vehicles are forming major sources of metallic nanoparticles into the environment and surrounding atmosphere [1, 2]. Most of these emissions are from Diesel engine vehicles either passengers or heavy-duty truck engines [3]. 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 [4, 5]. After long term exposure to Particulate Matter (PM) 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. The existing emission standards Euro 6 [6, 7], Tier 3 [8], or LEV III [9], for Diesel engine passenger vehicles specify the maximum allowable emissions of hydrocarbons, carbon monoxide, nitrogen oxides and for particulate matter, as the total number of all particles, from Diesel exhaust fumes. However, there are no specific emission standards for additional compounds or chemical elements contained in the exhaust emissions, particularly in exhaust vapour [10], particulates, particulate matter, Diesel Particulate Matter (DPM) [11], black carbon / carbon black (BC/CB), or in the soot [12], formed by the Diesel [13] or Biodiesel [14], from combustion engines. Even though chemical elements adsorbed to carbon particulates, present a significant fraction of total DPM or soot emission contents [15]. Therefore accurate in-situ technique to assess the on-line elemental composition analyses of particulate matter from automotive pollutant emissions would be desirable. The aim of this study is to use high resolution laser induced breakdown spectroscopy (LIBS) technique [16] for precise spectrochemical analytical characterisation of particulate matter emissions generated from in-use Diesel engine passenger vehicles.

2. Experiments

High resolution Laser Induced Breakdown Spectroscopy setup

Experimental laser induced breakdown spectroscopy setup for spectrochemical analytical studies of Diesel particulate matter collected from in-use Diesel combustion engine passenger vehicles consists of high intensity pulsed laser system Nd:YAG laser, with nanosecond laser pulse duration, experimental chamber, collimating and focusing optics and high precision optical spectrometer [17]. The plasma is generated by focusing high intensity laser pulse radiation into the target material. Usually a solid state laser or diode pumped laser is applied at its fundamental wavelength of 1064 nm or the second harmonic at 532 nm with repetition rates from 1 Hz to few kHz [18]. A schema of experimental LIBS setup is shown in Figure 1.

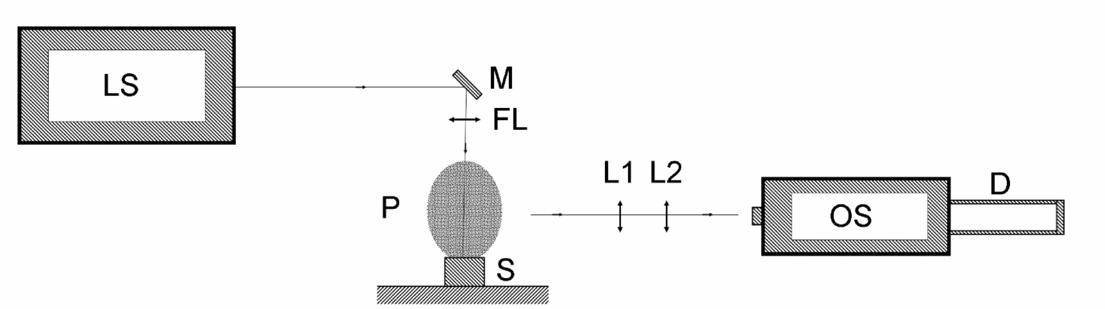

Figure 1. Layout of the Laser Induced Breakdown Spectroscopy experimental setup. LS - laser source (Nd:YAG laser, Yasmin, Quantel, France), M - Mirror, P - plasma, S - sample, FL - focusing lens, L1 and L2 - optical telescope, OS - optical spectrometer (Aryelle Butterfly, Echelle spectrograph, LTB Berlin, Germany), D - ICCD detector (PI-Max 4, Princeton Instruments, USA).

To generate the laser induced breakdown from Diesel particulate matter samples, Nd:YAG solid state laser - Yasmin, from Quantel, France has been used. It has been operated at the fundamental laser wavelength 1064nm with pulse duration 8.5ns and laser energy 300mJ per single pulse. Due to the large number and different origin of DPM matrices, we applied higher laser energy, to enhance the optical emission from the plasma and gain signals from the infrared, visible as well as ultraviolet spectral region. The laser radiation has been focused with a 10 cm focusing lens into the plane DPM solid target surface to create a plasma. Optical emissions from the plasma have been collected perpendicularly, via an optical telescope, into the high resolution Echelle spectrograph, model Aryelle Butterfly from LTB Lasertechnik Berlin, Germany equipped with an ICCD detector PI-Max 4 from Princeton Instruments, USA. The spectrometer consists of two separate spectrographs, one for the UV range from 190nm to 440nm and the second unit for VIS optical spectrum in a range from 440nm to 800nm. The spectral resolution capability is from 3 pm to 7 pm (pm = picometre) for the UV range and from 4 pm to 8 pm for the VIS range, thus providing spectral information of a broad range with very high resolution and variability. Optical emissions from the plasma have been collected from ultraviolet to infrared spectral window, thus the total spectrum from 190nm to 800nm has been recorded. The delay time for starting recording of the optical spectral signal has been set to 1μs after the trigger signal, and gate time for spectral acquisition has been set to 2μs. In earlier delay times than 1μs, the black body radiation is dominating in the laser induced plasma, while for later time intervals like 3μs the atomic and ionic emissions start decaying [19]. The LIBS emission has been measured in open air atmosphere at atmospheric pressure and room temperature.

3. Results

3.1 Major chemical elements in Diesel Particulate Matter

Major chemical elements in Diesel Particulate Matter were obtained by Laser Induced Breakdown Spectroscopy setup shown in previous chapter. Examples of measured LIBS spectra from different Diesel Particulate Matter samples are shown in Figure 2. In this figure, x-axis represents the measured spectral wavelength and the y-axis represents the intensity of measured spectral LIBS signal, in the arbitrary units (a.u.). Arbitrary units are used due to the lack of absolute intensity signal. Therefore, this is the reason why in practice, the LIBS signal has to be further calibrated. Measured laser induced breakdown optical spectra obtained from DPM exhibits typical line spikes with distinct line peaks, generated from atomic, ionic and molecular spectral transitions corresponding to different chemical elements. In Figure 2 spectrographs we can observe strong optical line emission mainly from major chemical elements: in spectrum **a)** Ca, Mg, Zn; in spectrum **b)** Ca, Cr, Fe, H, Mg, Na and in spectrum **c)** Al, C, Ca, Cr, Mg, O.

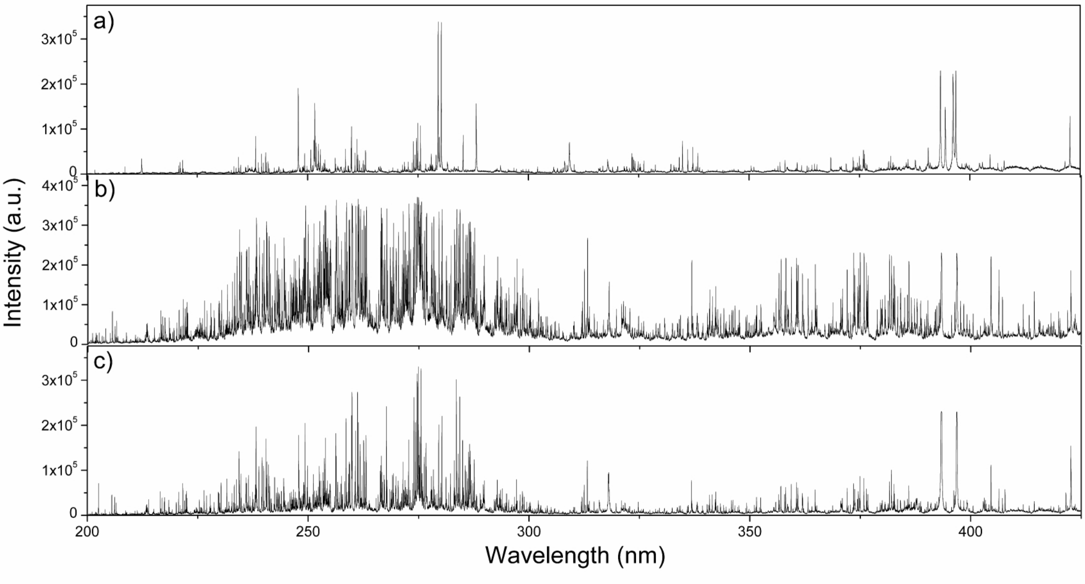

Figure 2. Laser Induced Breakdown Spectroscopy signal measured from three different Diesel Particulate Matter samples. Intense spectral lines are from major chemical elements - spectrum **a)** Ca, Mg, Zn; spectrum **b)** Ca, Cr, Fe, H, Mg, Na and spectrum **c)** Al, C, Ca, Cr, Mg, O.

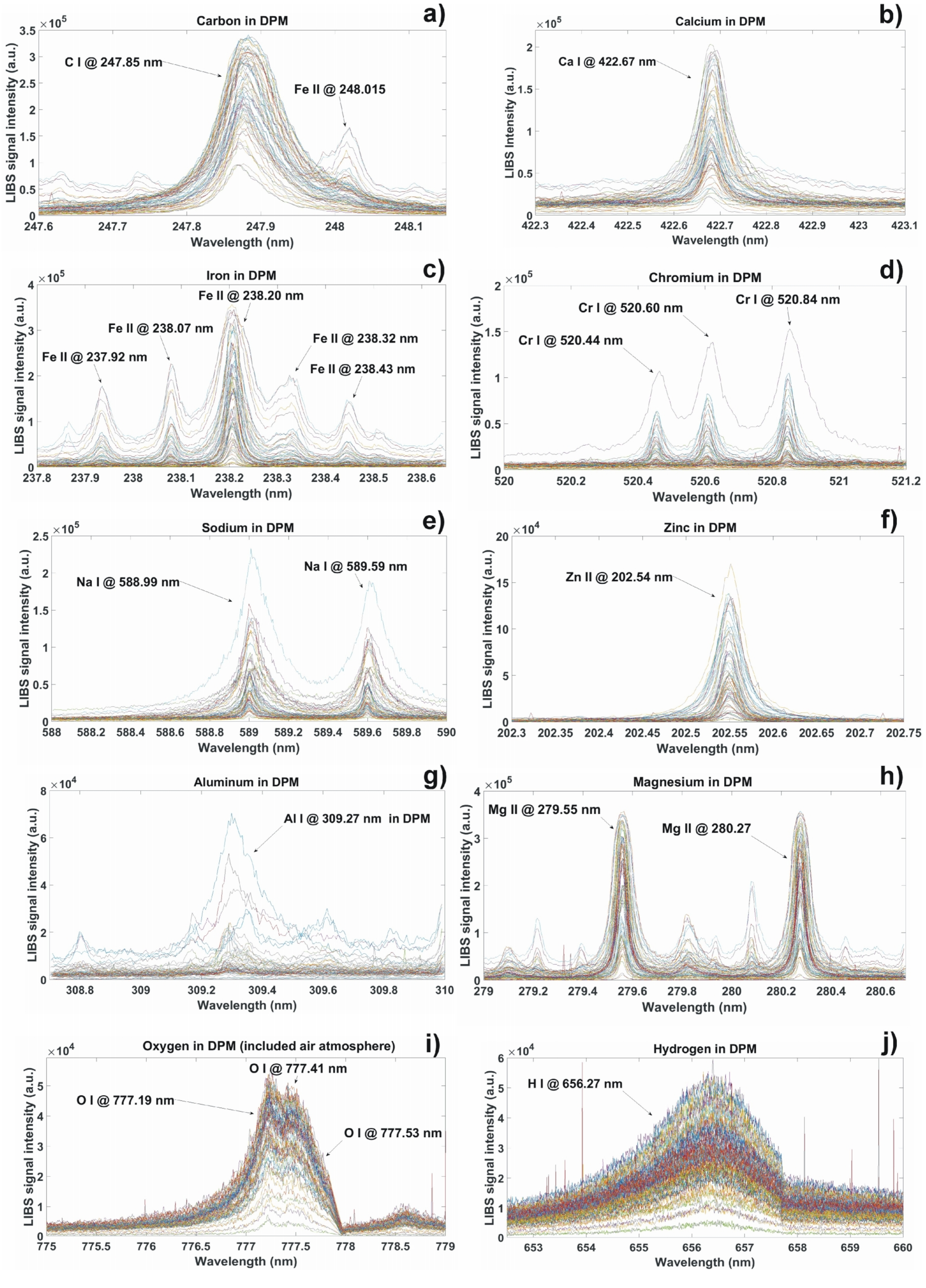

Figure 3. High resolution LIBS spectra from 67 samples of Diesel Particulate Matter extracted from in-use Diesel engine passenger vehicles. Optical emission is from major chemical elements: Carbon (a), Calcium (b), Iron (c), Chromium (d), Sodium (e), Zinc (f), Aluminium (g), Magnesium (h), Oxygen (i) and Hydrogen (j).

In Figure 3 are shown high resolution LIBS spectral data from 67 samples of Diesel Particulate Matter extracted from in-use Diesel engine passenger vehicles. Spectra are from most abundant lines from major chemical elements: Carbon (a), Calcium (b), Iron (c), Chromium (d), Sodium (e), Zinc (f), Aluminium (g), Magnesium (h), Oxygen (i) and Hydrogen (j) spectral lines. Measured chemical elements were in our previous publications characterised as major components of Diesel Particulate Matter. More details related to this study are explained in the references [15, 20].

3.2 Minor chemical elements in Diesel Particulate Matter

In order to spectroscopicaly characterise the minor chemical elements in Diesel Particulate Matter, state-of-the-art laboratory LIBS setup was build to obtain optical emission spectral images with high spectral resolution. The results from these measurements are shown in Figure 4. In this figure, x-axis represents measured wavelength of peak spectral signal and y-axis represents the intensity of LIBS signal in arbitrary units. Here we mainly focus our research to minor chemical elements. These are particularly minor spectral lines from Silicon, Nickel, Titan, Potassium, Strontium and Molybdenum atomic or ionic optical emission.

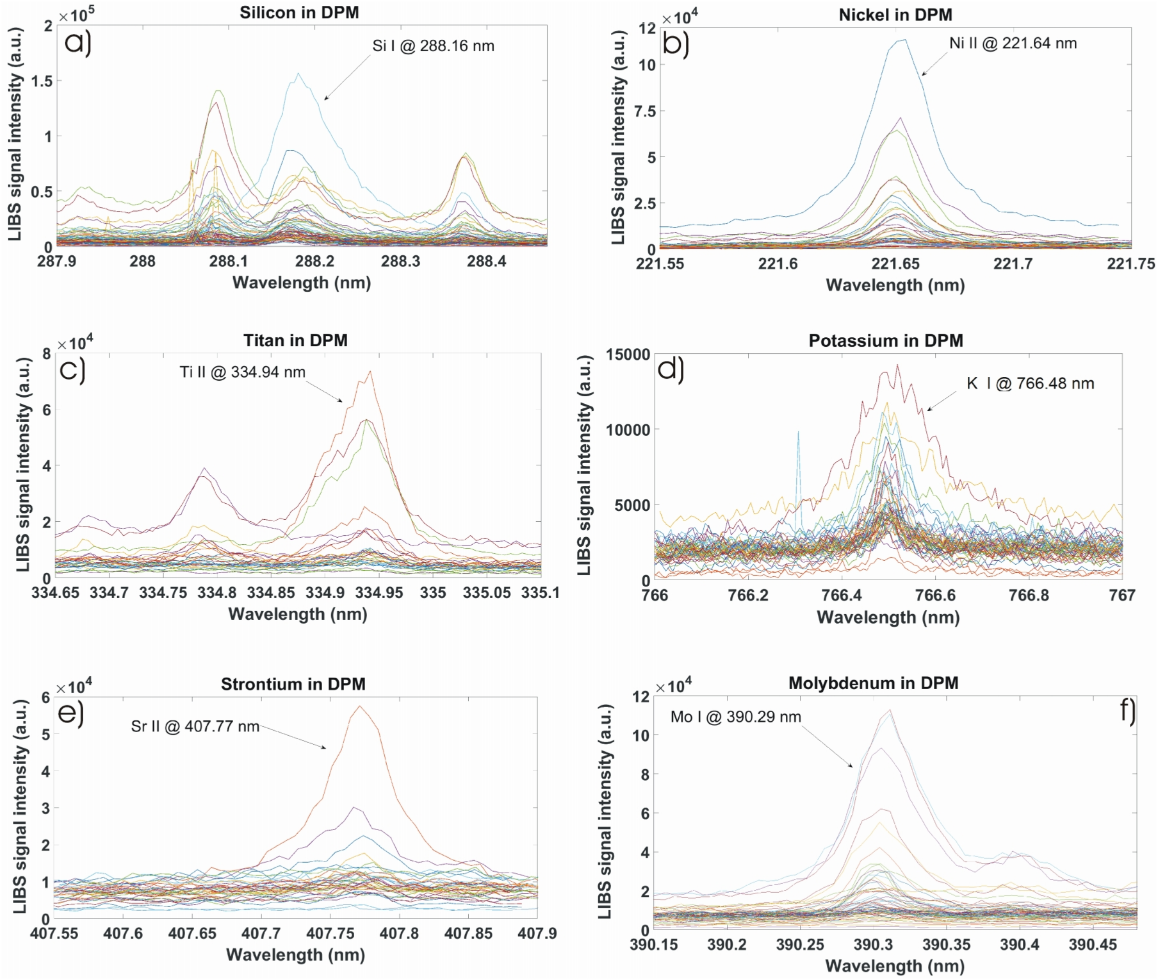

Figure 4. Optical emission from minor chemical elements measured by LIBS from different Diesel Particulate Matter samples. Spectrum from: a) Silicon, b) Nickel, c) Titan, d) Potassium, e) Strontium and f) Molybdenum.

4.3 Trace chemical elements in Diesel Particulate Matter

To identify trace elements in various DPM matrices, optical detection of LIBS setup was further optimised, to obtain good quality signal to noise spectral signal.

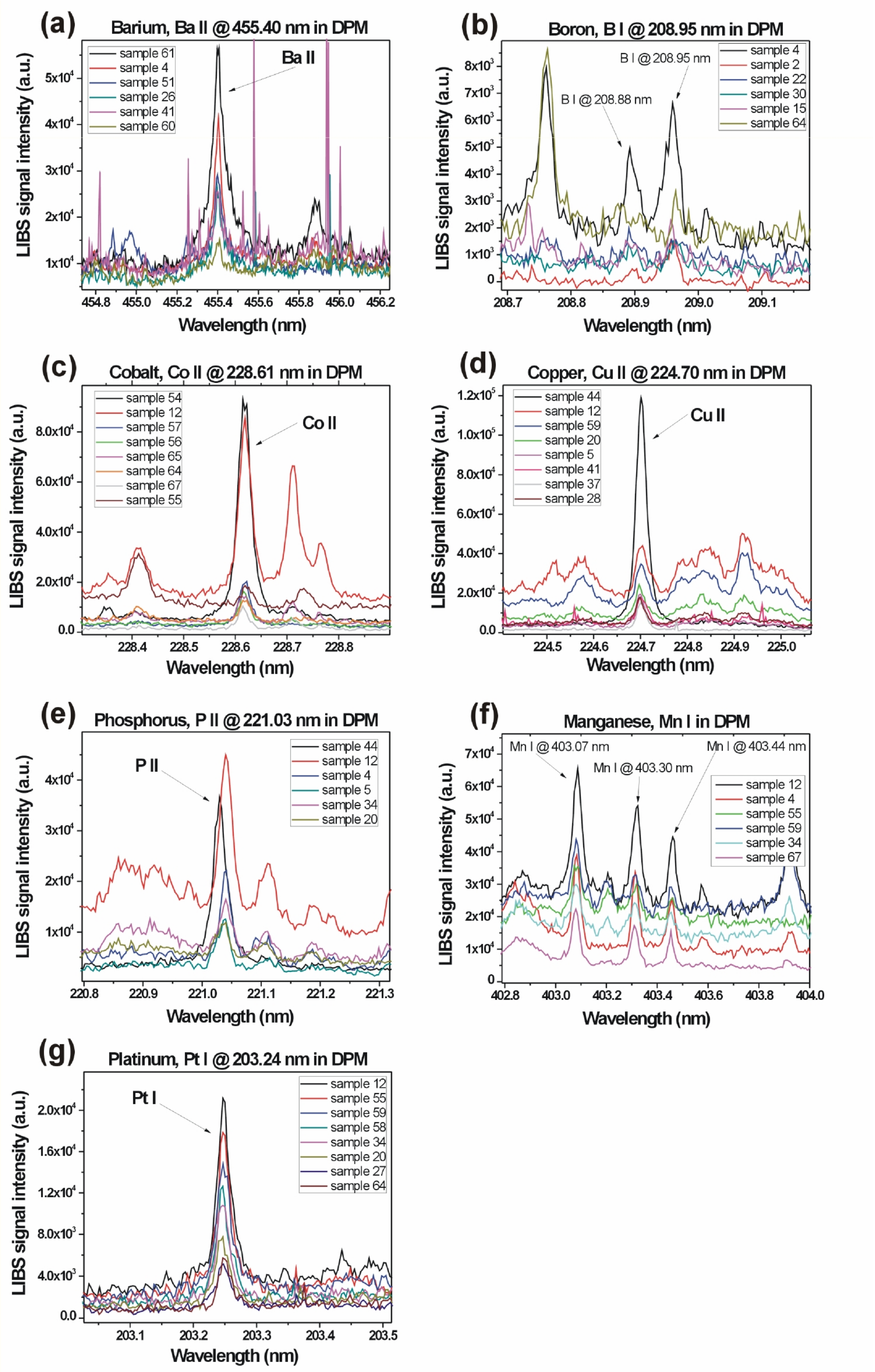

Figure 5. Optical emission spectra from trace elements: Barium (a), Boron (b), Cobalt (c), Copper (d), Phosphorus (e), Manganese (f) and Platinum (g), measured by high resolution LIBS technique from Diesel particulate matter collected from in-use passenger Diesel engine vehicles.

Optical emission spectra from atomic and ionic lines of selected trace elements in DPM are shown in Figure 5. These signal peaks are particularly from: Barium (a), Boron (b), Cobalt (c), Copper (d), Phosphorus (e), Manganese (f) and Platinum (g). Here we only select few DPM samples with pronounced LIBS signal, to clearly interpret measured results from trace elements.

4. Discussion

In this study we shortly shown LIBS technique for sensitive measurements of major, minor and trace chemical elements contained in the Diesel particulate matter. From obtained data we can summarise that the Laser Induced Breakdown Spectroscopy technique can sensitively identify chemical elements in particulate matter. LIBS can provide qualitative as well as quantitative analyses of chemical composition of DPM. The exact composition of DPM exhaust emissions from in-use Diesel engine passenger vehicles is related to different processes involved during the engine combustion as well as applied exhaust filtering devices. Due to complex processes involved within the combustion, agglomeration of chemical elements in exhaust emissions occurred. These processes depend on engine type, engine size, engine operation conditions, type of fuel, quality of fuel, additives, lubricants and aftertreatment devices. All these devices and conditions modify the exhaust emissions and final chemical composition of emitted PM from in-use Diesel engine vehicles. Up to now, it is not distinct which of these sources are mostly influencing the composition of DPM.

5. Conclusions

To summarise, in this proceeding we have shown the spectrochemical characterisation of particulate matter emissions generated from in-use Diesel engine vehicles. We have extracted Diesel Particulate Matter from the end part of the tail pipe, from more than seventy different vehicles. Afterwards in laboratory we have used the high resolution laser induced plasma spectroscopy (LIBS) spectrochemical analytical technique to sensitively analyse chemical elements in different DPM. We have found that PM 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. Beside the major elements of DPM there are also minor chemical elements: Silicon, Nickel, Titan, Potassium, Strontium, Molybdenium and others. 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.

In future, we would like to identify individual sources of major, minor and trace chemical components of DPM exhaust emissions. It is important to understand from where these elements are coming from. The further classification of primary sources responsible for these metallic nanoparticles in Diesel particulate matter would be an asset. 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.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ntziachristos, L.; Papadimitriou, G.; Ligterink, N.; Hausberger, S. Implications of Diesel emissions control failures to emission factors and road transport NOx evolution. *Atmos. Environ.* **2016**, *141*, 542–551, doi:10.1016/j.atmosenv.2016.07.036.
2. Zacharof, N.; Tietge, U.; Franco, V.; Mock, P.: Type approval and real-world CO2 and NOx emissions from EU light commercial vehicles. *Energy Policy* **2016**, *97*, 540–548, doi:10.1016/j.enpol.2016.08.002.
3. Commission Regulation (EU) 2016/646. Commission Regulation (EU) 2016/646 of 20 April 2016 Amending Regulation (EC) (No 692/2008) as Regards Emissions from Light Passenger and Commercial Vehicles (Euro 6). Available online: http://eur-lex.europa.eu/eli/reg/2016/646/oj (accessed on 9. January 2020).
4. Calderón-Garcidueñas, L.; Mora-Tiscareño, A.; Ontiveros, E.; Gómez-Garza, G.; Barragán-Mejía, G.; Broadway, J.; Chapman, S.; Valencia-Salazar, G.; Jewells, V.; Maronpot, R.R.; et al. Air pollution, cognitive deficits and brain abnormalities: A pilot study with children and dogs. *Brain Cogn.* **2008**, *68*, 117–127, doi:10.1016/j.bandc.2008.04.008.
5. Block, M.L.; Calderon-Garciduenas, L. Air pollution: Mechanisms of neuroinflammation and CNS disease *Trends Neurosci.* **2009**, *32*, 506–516, doi:10.1016/j.tins.2009.05.009.
6. Commission Regulation (EC) 692/2008. Commission Regulation (EC) 692/2008 of 18 July 2008 Implementing and Amending 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. Available online: http://eur-lex.europa.eu/eli/reg/2008/692/oj (accessed on 9. January 2020).
7. Regulation (EC) No 715/2007. Regulation (EC) No 715/2007 of the European Parliament and of the Council of 20 June 2007 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. Available online: http://eur-lex.europa.eu/eli/reg/2007/715/oj (accessed on 9. January 2020)
8. United States Environmental Protection Agency, Regulations for Emissions from Vehicles and Engines, Tier 3 Motor Vehicle Emission and Fuel Standards. Available online: https://www.epa.gov (accessed on 9. January 2020)
9. California Environmental Protection Agency, Low-Emission Vehicle Program-LEV III. Available online: https://www.arb.ca.gov/ (accessed on 9. January 2020)
10. Lough, G. C.; Schauer, J. J.; Park, J. S.; Shafer, M. M.; Deminter, J. T.; Weinstein, J. P.; *Environ. Sci. Technol.* **2005,** *39*, 826.
11. Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T.; *Environ. Sci. Technol.* **1999**, *33*, 1578.
12. Cheung, K. L.; Ntziachristos, L.; Tzamkiozis, T.; Schauer, J. J.; Samaras, Z.; Moore, K. F.; Sioutas, C.; *Aerosol Sci. Technol.* **2010**, *44*, 500.
13. Tolomelli, L. T. E.; Barreta, L. G.; Lacava, P. T.; Carinhana, D.; *J. Braz. Chem. Soc.* 2017, *28*, 1384**.**
14. Das, D.; Kumar A.; Yadav A.; *Biofuels* **2018**, *9*, 89.
15. 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

16. Noll, R. *Laser-Induced Breakdown Spectroscopy, Fundamentals and Applications*; Springer-Verlag: Berlin, Germany, 2012.
17. Miziolek, A.W.; Palleschi, V.; Schechter, I. *Laser-Induced Breakdown Spectroscopy (LIBS): Fundamentals and Application*; Cambridge University Press: New York, NY, USA, 2006.
18. Cremers, D.A.; Radziemski, L.J. *Handbook of Laser-Induced Breakdown Spectroscopy*; John Wiley & Sons Inc.: New Delhi, India, 2013.
19. 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.
20. 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.