environmental sciences proceedings

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Proceeding Paper

Spectrochemical Analytical Characterisation of Particulate Matter Emissions Generated from In-Use Diesel Engine Vehicles

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† Presented at the 3rd International Electronic Conference on Atmospheric Sciences, 16–30 November 2020; Available online: https://ecas2020.sciforum.net/.

Abstract: Pollutant emissions from vehicles form major sources of metallic nanoparticles entering the environment and surrounding atmosphere. In this research, we spectrochemically analyse the chemical composition of particle matter emissions from in-use diesel engine passenger vehicles. We extracted diesel particulate matter from the end part of the tail pipes of more than 70 different vehicles. In the laboratory, we used the high-resolution laser-induced breakdown spectroscopy (LIBS) spectrochemical analytical technique to sensitively analyse chemical elements in different DPM samples. We found that PM is composed of major, minor and trace chemical elements. The major compound in PM is not strictly carbon but also other adsorbed metallic nanoparticles such as iron, chromium, magnesium, zinc and calcium. Besides the major elements in DPM, there are also minor elements: silicon, nickel, titan, potassium, strontium, molybdenum and others. Additionally, in DPM are adsorbed atomic trace elements like barium, boron, cobalt, copper, phosphorus, manganese and platinum. All these chemical elements form the 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 emissions; epidemiology; toxicology; optical emission spectroscopy; laser-induced breakdown spectroscopy; laser-induced plasma spectroscopy; LIBS; LIPS

Citation: Viskup, R.; Vereshchaga, Y.; Stadler, A.T.; Roland, T.; Wolf, C.; Weth, A.; Baumgartner, W. Spectrochemical Analytical Characterisation of Particulate Matter Emissions Generated from In-Use Diesel Engine Vehicles. *Environ. Sci. Proc.* **2021**, *4*, 18. https://doi.org/10.3390/ecas2020-08468

Academic Editor: Anthony R. Lupo

Published: 17 November 2020

1. Introduction

Pollutant emissions from vehicles form major sources of metallic nanoparticles entering the environment and surrounding atmosphere [1,2]. Most of these emissions are from diesel engine vehicles, either passenger vehicles or heavy-duty trucks [3]. For human health, it is important to breathe clean, non-polluted air, not only for the 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 pulmonary diseases, 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 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 exhaust emissions, particularly in exhaust vapour [10], particulates, particulate matter, diesel particulate matter (DPM) [11], black carbon/carbon black (BC/CB) or soot [12], formed by the diesel [13] or biodiesel [14] in combustion engines, even though chemical elements adsorbed to carbon particulates present a significant fraction of the total DPM or soot emission contents [15]. Therefore, an accurate in situ technique to assess the on-line elemental composition of particulate matter in automotive pollutant emissions would be desirable. The aim of this study was to use the 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 Set-Up

The experimental laser-induced breakdown spectroscopy set-up 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 a nanosecond laser pulse duration, an experimental chamber, collimating and focusing optics and a high-precision optical spectrometer [17]. The plasma is generated by focusing high-intensity laser pulse radiation into the target material. Usually, 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 a few kilohertz [18]. A schema of the experimental LIBS set-up is shown in Figure 1.

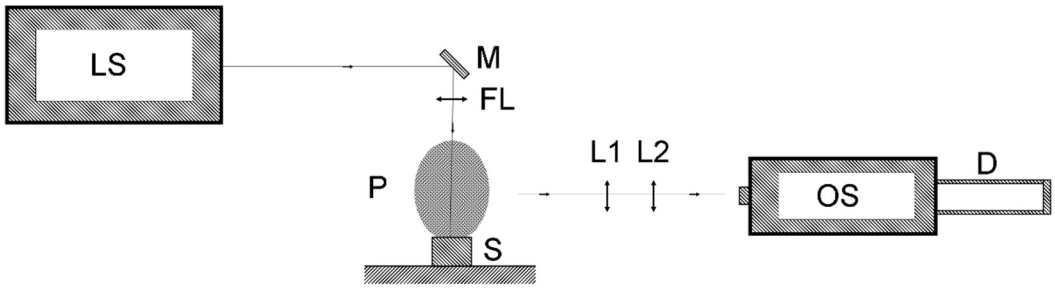

Figure 1. Layout of the laser-induced breakdown spectroscopy experimental set-up. LS—laser source (Nd:YAG laser, Yasmin, Quantel, France); M—mirror; P—plasma; S—sample; FL—focusing lens; L1 and L2—optical telescope; OS—optical spectrometer (Aryelle Butterfly, Echelle spectrograph, LTB Berlin, Germany); D— Intensified Charge Coupled Device (ICCD) detector (PI-Max 4, Princeton Instruments, Trenton, NJ, USA).

To generate the laser-induced breakdown of diesel particulate matter samples, Nd:YAG solid-state laser (Yasmin, Quantel, France) was used. It was operated at the fundamental laser wavelength of 1064 nm with pulse duration 8.5 ns and laser energy 300 mJ per 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 was focused with a 10 cm focusing lens into the plane DPM solid target surface to create a plasma. Optical emissions from the plasma were collected perpendicularly, via an optical telescope, into the high-resolution Echelle spectrograph (model Aryelle Butterfly from LTB Lasertechnik Berlin, Germany) equipped with an Intensified Charge Coupled Device (ICCD) detector PI-Max 4 from Princeton Instruments, USA. The spectrometer consists of two separate spectrographs, one for the UV range from 190 to 440 nm and the second unit for the VIS optical spectrum in a range from 440 to 800 nm. The spectral resolution capability is from 3 to 7 picometre (pm) for the UV range and from 4 p.m. to 8 p.m. for the VIS range, thus providing spectral information about a broad range with high resolution and

variability. Optical emissions from the plasma were collected from the ultraviolet-to-infrared spectral window; thus the total spectrum from 190 nm to 800 nm was recorded. The delay time for starting the recording of the optical spectral signal was set to 1 μs after the trigger signal, and the gate time for spectral acquisition was set to 2 μs. In delay times earlier than 1 μs, the black-body radiation dominates in the laser-induced plasma, while for later time intervals, like 3 μs, the atomic and ionic emissions start decaying [19]. The LIBS emission was measured in an open-air atmosphere at atmospheric pressure and room temperature.

3. Results

3.1. Major Chemical Elements in Diesel Particulate Matter

The major chemical elements in diesel particulate matter were obtained by the laser-induced breakdown spectroscopy set-up shown in the previous section. Examples of measured LIBS spectra from different diesel particulate matter samples are shown in Figure 2. In this figure, the x axis represents the measured spectral wavelength and the y axis represents the intensity of the measured spectral LIBS signal in arbitrary units (a.u.). Arbitrary units are used due to the lack of an 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 exhibit typical line spikes with distinct line peaks, generated from atomic, ionic and molecular spectral transitions corresponding to different chemical elements. In the Figure 2 spectrographs, we can observe strong optical line emissions mainly from major chemical elements: in spectrum (a), Ca, Mg and Zn; in spectrum (b), Ca, Cr, Fe, H, Mg and Na; and in spectrum (c), Al, C, Ca, Cr, Mg and O.

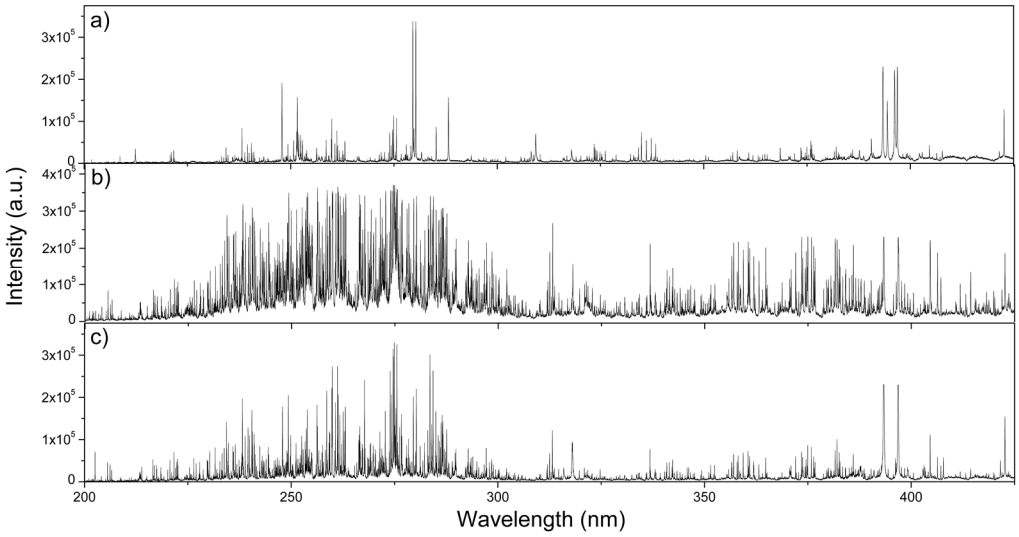

Figure 2. Selected LIBS signal measured from three different diesel particulate matter samples. Intense spectral lines are from major chemical elements—spectrum (**a**) Ca, Mg, Zn; spectrum (**b**) Ca, Cr, Fe, H, Mg, Na; and spectrum (**c**) Al, C, Ca, Cr, Mg, O.

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 the 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. The measured chemical elements were characterised as major components of diesel particulate matter in our previous publications. More details related to this study are explained in [15,20].

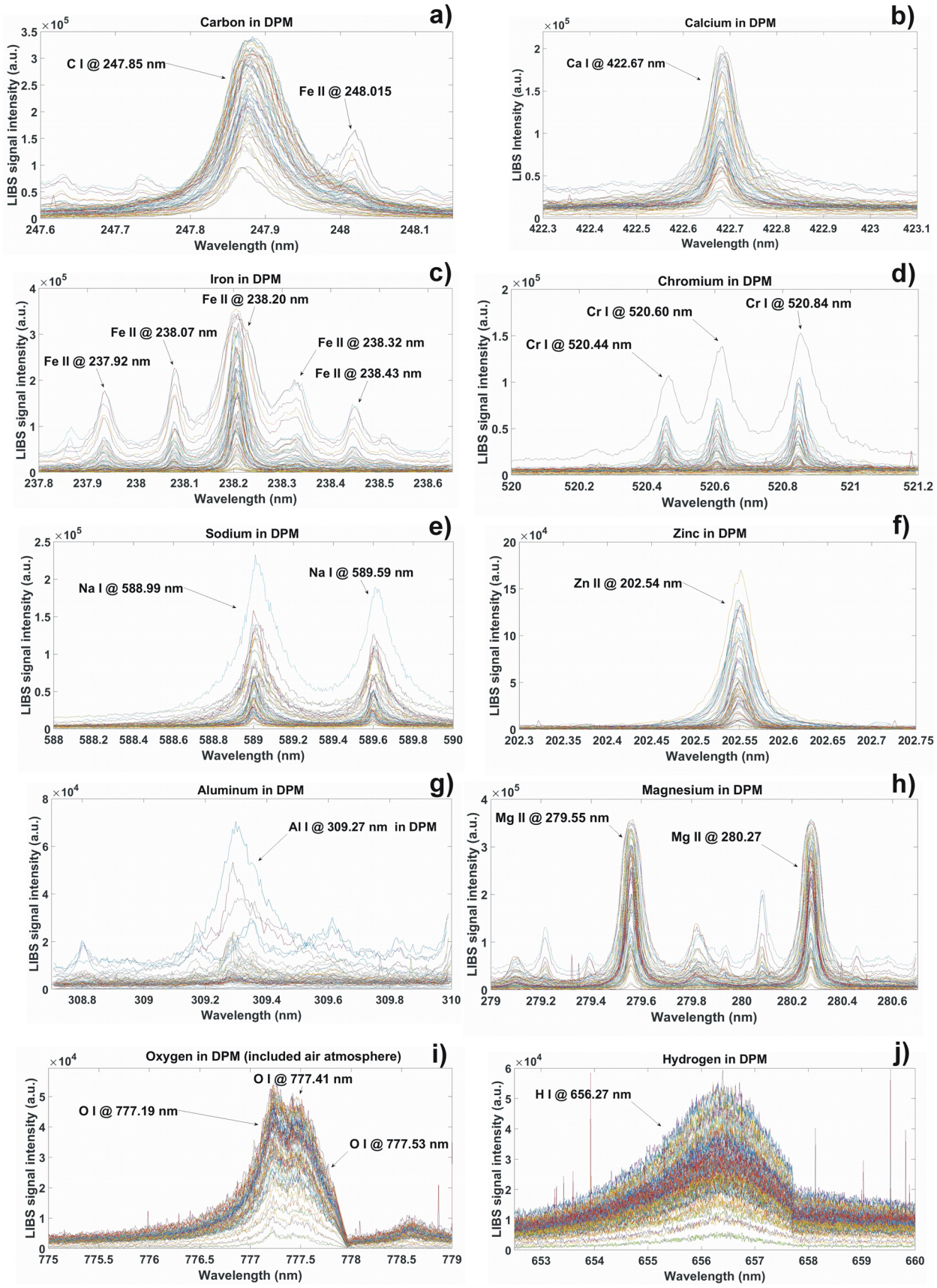

Figure 3. High-resolution laser-induced breakdown spectroscopy (LIBS) spectra from 67 samples of diesel particulate matter extracted from in-use diesel engine passenger vehicles. Optical emission is from major chemical elements: (**a**) carbon, (**b**) calcium, (**c**) iron, (**d**) chromium, (**e**) sodium, (**f**) zinc, (**g**) aluminium, (**h**) magnesium, (**i**) oxygen and (**j**) hydrogen.

3.2. Minor Chemical Elements in Diesel Particulate Matter

To spectroscopically characterise the minor chemical elements in diesel particulate matter, a state-of-the-art laboratory LIBS set-up was built to obtain optical emission spectral images with high spectral resolution. The results from these measurements are shown in Figure 4. In this figure, the x axis represents the measured wavelength of the peak spectral signal and the y axis represents the intensity of the LIBS signal in arbitrary units. Here, we mainly focus our research on minor chemical elements in DPM. We identified minor spectral lines from silicon, nickel, titan, potassium, strontium and molybdenum atomic or ionic optical emissions. Different concentrations of detected minor elements were measured with respect to the type of complex particulate matter, this topic is further discussed in our publications [21,22].

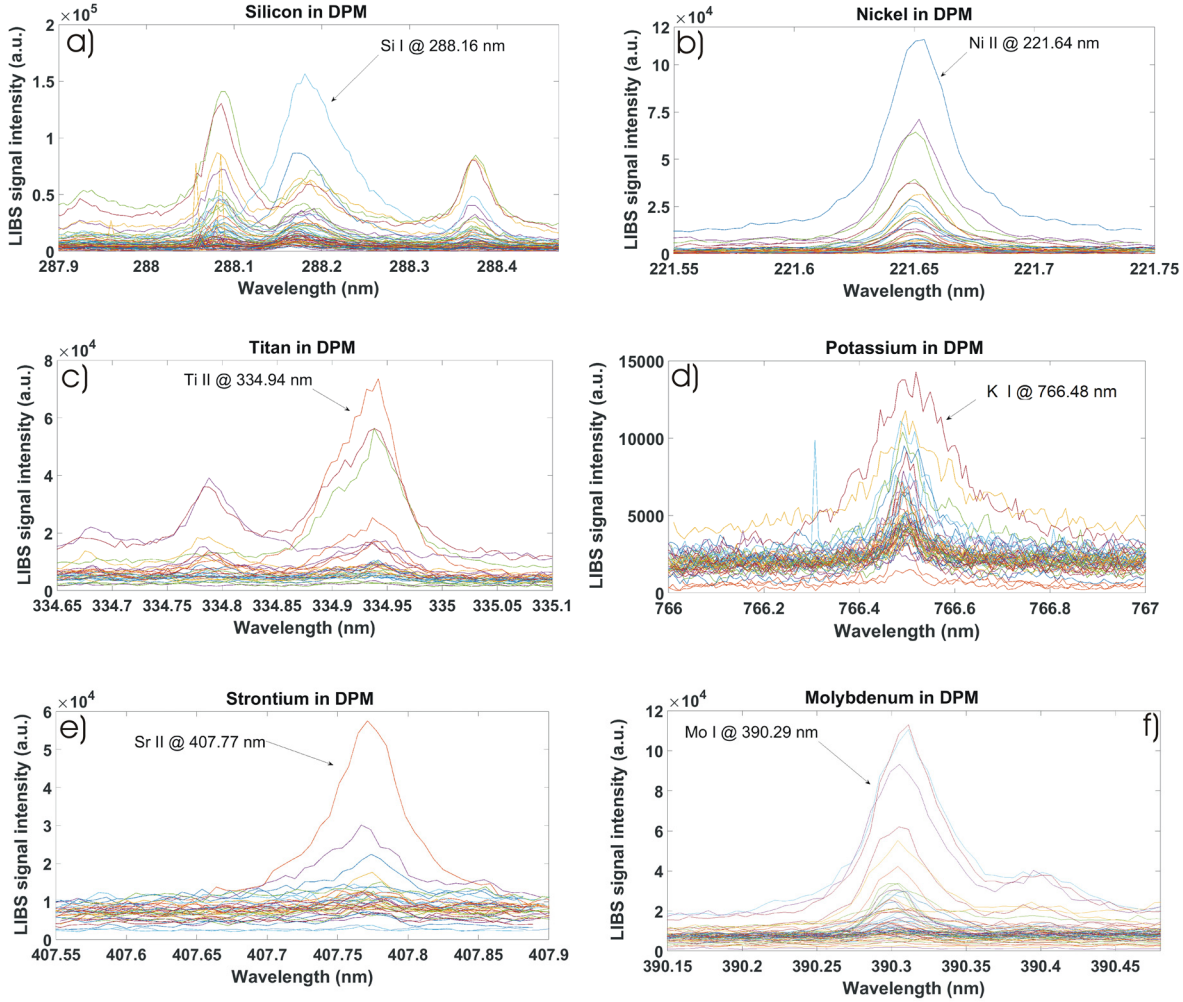

Figure 4. Optical emission from minor chemical elements measured by LIBS from different diesel particulate matter samples. Spectra from (**a**) silicon, (**b**) nickel, (**c**) titan, (**d**) potassium, (**e**) strontium and (**f**) molybdenum.

3.3. Trace Chemical Elements in Diesel Particulate Matter

To identify trace elements in various DPM matrices, the optical detection of the LIBS set-up was further optimised to obtain a good-quality signal. 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 a few DPM samples with a pronounced LIBS signal to clearly interpret measured results from trace elements. Further

detail study related to this subject is described in our publication - Qualitative characterisation of trace elements in Diesel Particulate Matter from in-use diesel engine passenger vehicles by means of laser-induced breakdown spectroscopy technique in [23].

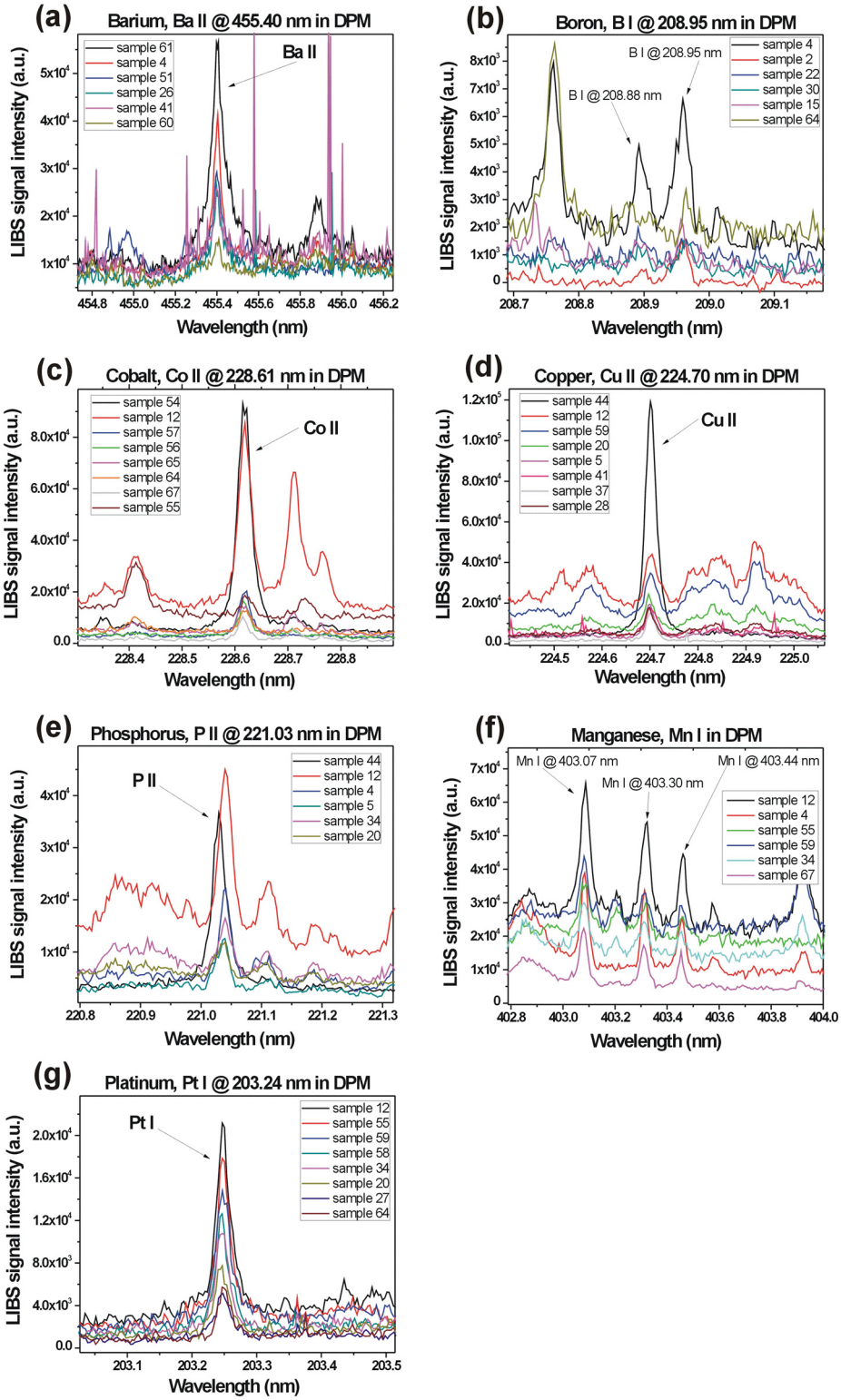

Figure 5. Optical emission spectra from trace elements: (**a**) barium, (**b**) boron, (**c**) cobalt, (**d**) copper, (**e**) phosphorus, (**f**) manganese and (**g**) platinum. These were measured by the high-resolution LIBS technique from diesel particulate matter samples collected from in-use diesel engine passenger vehicles.

4. Discussion

In this study, we shortly showed the LIBS technique for sensitive measurements of major, minor and trace chemical elements contained in diesel particulate matter. From the 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 the 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 engine combustion as well as applied exhaust filtering devices. Due to the complex processes involved in combustion, agglomeration of chemical elements in exhaust emissions occurs. These processes depend on the engine type, engine size, engine operation conditions, type of fuel, quality of fuel, fuel additives, engine lubricants, pre- treatment and after-treatment devices. All these factors and engine conditions modify exhaust emissions and the final chemical composition of emitted PM from in-use diesel engine vehicles. Up to now, it is not distinct which of these sources mostly influence the composition of DPM.

5. Conclusions

To summarise, in this proceeding, we showed the spectrochemical characterisation of particulate matter emissions generated from in-use diesel engine vehicles. We extracted diesel particulate matter from the end part of the tail pipes of more than 70 different vehicles. Afterwards, in the laboratory, we used the high-resolution laser-induced breakdown spectroscopy (LIBS) spectrochemical analytical technique to sensitively analyse chemical elements in different DPM samples. We found that PM is composed of major, minor and trace chemical elements. The major compound of DPM is not strictly carbon, but other adsorbed nanoparticles such as iron, chromium, aluminium, zinc, magnesium, calcium, sodium, oxygen and hydrogen. Besides the major elements in DPM, there are also minor chemical elements: silicon, nickel, titan, potassium, strontium, molybdenum and others. Additionally, in DPM are adsorbed atomic trace elements: barium, boron, cobalt, copper, phosphorus, manganese and platinum. All these chemical elements form the significant atomic composition of real particulate matter from in-use diesel engine passenger vehicles.

In the 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 originate. A further classification of primary sources responsible for these metallic nanoparticles in diesel particulate matter would be an asset. All this information will be helpful for developing a LIBS method as an accurate in-situ technique for online / offline elemental composition analyses of particulate matter emissions from vehicles and hence for minimising pollutant emissions from in-use diesel-engine-driven vehicles.

Author Contributions: All authors contributed to the manuscript. For further details, please contact the corresponding author.

Funding: Authors would like to thank the Linz Center of Mechatronics (LCM), project number K 24400/LCM, for financial support. This research was funded by the Austrian Science Fund (Fonds zur Förderung der wissenschaftlichen Forschung) FWF, project number P 27967.

Acknowledgments: Authors would like to thank Maria Rusnak for proofreading and for valuable corrections and open access funding by the Austrian Science Fund (Fonds zur Förderung der wissenschaftlichen Forschung) FWF (P 27967). Authors would also like to acknowledge the financial support of the Linz Center of Mechatronics (LCM), project number K 24400/LCM.

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

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