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Chapter

Identification of the Minor Chemical Elements in the Particulate Matter Exhaust Emissions From In-Use Diesel Engine Passenger Vehicles

Richard Viskup, Christoph Wolf and Werner Baumgartner

Abstract

In this research, we investigate the minor chemical elements contained in the particulate matter (PM) exhaust emissions, generated by in-use diesel engine passenger vehicles. For this purpose, we apply a high-resolution optical emission spectroscopy technique, for precise, spectrochemical analysis of diesel particulate matter (DPM). By means of the laser-induced breakdown spectroscopy analytical method, we analyse PM from different road diesel engine vehicles. DPM were obtained from miscellaneous in-use diesel engine passenger vehicles of diverse types and models from major brand car producers in Europe. We analysed particulate matter extracted from the exhaust manifold part, from 67 different passenger vehicles, which are used in daily life environment.

Keywords: laser-induced breakdown spectroscopy, LIBS, laser-induced plasma spectroscopy, LIPS, particulate matter, particulates, soot, carbon emissions, vehicle emissions, exhaust emissions, ultrafine particles, metallic nanoparticles, trace metals, trace elements, trace emission, air quality

1. Introduction

Problems with diesel engine emissions and control failures [1–3] are present in public perception around the world. To breathe clean air is very important for human health not only for lungs and cardiovascular system, but also for the brain and central nervous system [4, 5]. Therefore, it should be amongst our highest priorities to find new techniques and technology to successfully solve the emission issues.

In this study, we applied a laser-induced breakdown spectroscopy technique [6] for qualitative spectrochemical analysis of diesel particulate matter (DPM) emitted from in-use diesel engine passenger vehicles.

We analysed particulate matter from 67 different diesel engine passenger vehicles of major EU car producers, used in daily life environment. The aim of this study is to compare particulate matter (PM) composition, mainly agglomerated minor chemical elements. Special attention is given to the analysis of different PM

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for a qualitative comparison of the Laser induced breakdown spectroscopy (LIBS) spectral signal. The presence of agglomerate chemical elements in diesel exhaust emissions is due to different processes involved within the combustion. These are mainly related to the diesel fuel, fuel additives, engine lubricants, engine performance, applied aftertreatment devices like selective catalytic reduction devices and diesel particulate filtering techniques. All these input parameters influence the final chemical composition of exhaust emissions and consequently the diesel particulate matter emitted from in-use diesel engine vehicles.

The current existing emission standards in the European Union, like European emission standards – Euro [7, 8], or in USA – Tier [9], or LEV [10], for diesel engine vehicles specify the maximum allowable emissions of hydrocarbons, carbon monoxide, nitrogen oxides, and particulate matter (PM). PM is measured as the total number of all generated particles from diesel exhaust, expelled from diesel exhaust fumes. Currently, there are no specific emission standards for additional compounds or chemical elements contained in the exhaust emissions, i.e., exhaust vapour, diesel particulate matter, particulate matter, black carbon, or in the soot, formed by the diesel or biodiesel, from internal combustion engines. The agglomerated chemical elements in diesel particulate matter additional to carbon, presents a very large fraction of the total DPM or soot emission contents. Particularly, the inhalation of metal dusts and ions has numerous negative health effects, especially upon long-term exposure. Automotive emissions are considered as the dominant source for air-borne metal pollution in urban areas. Therefore, accurate in-situ technique to assess the on-line elemental composition of particulate matter from automotive emissions would be desirable.

Generally, exhaust emissions from diesel engines can form a very complex mixture of gases, vapour, and particles consisting of countless elements and compounds. Gaseous compounds of diesel emission include carbon dioxide, oxygen, nitrogen, water vapour, carbon monoxide, nitrogen compounds, sulphur compounds, and numerous low molecular weight compounds [11]. The vapour phase contains larger molecular weight compounds, located in unburned tailpipe emissions. The diesel exhaust particles are agglomerates of many primary spherical particles that differ in size [12], composition [13], and solubility [14]. The particles in diesel exhaust emission consist of particulate matter – diesel particulate matter. This is further classified, depending on the size of particles as particulates of an aerodynamic diameter of less than 10 μm, fine particles of diameters below 2.5 μm, ultra-fine particles – below 0.1 μm, and nanoparticles – characterised by diameter less than 50 nm. DPM is composed of elemental carbon in core and adsorbed compound. The elemental carbon core has a high specific surface area and serves as a nucleus for condensation of compounds with good adsorption properties mainly from the unburned or incompletely burned diesel, particles or from crankcase oil volatilised metallic nano-particles from the cylinder walls.

Amongst the early pioneers in measurement of particulate trace emissions from vehicles was the group of Schauer et al. [15] as they used a comprehensive dilution source sampler, organic chemical analysis, and X-ray fluorescence analysis for mass and chemical composition measurements of fine particles. Other groups [13, 16–18], used inductively-coupled plasma mass spectrometry ICP-MS and XRF for characterisation of metals and other particle-phase species from on-road motor vehicles. They found the following trace elements in the particles: Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Pt, S, Sr, Ti, V and Zn.

Other groups [19–23], used ICP-OES to characterise the different biodiesel samples with special concern to quantify the Al, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, P, Sr, B and Cl content, to evaluate the fuel quality and to control the emission of pollutants to the atmosphere. In this case, the samples were prepared using a high

pressure ashier digestion procedure for metal determination in biodiesel samples. Different groups used ICP-MS to characterise additional bound elements, like Cd, As, Ba and Ti in the particulate matter collected from ultra-low sulphur diesel and biodiesel-powered engine exhaust emissions [24].

The first pioneering group investigated the metallic elements in diesel soot collected on filter by means of laser-induced breakdown spectroscopy was by Lombaert et al. [25]. They found that Fe, Cu, Ca, Zn and Mg appear as the main metallic species deposited within diesel particles on the reference filter.

The qualitative and quantitative characterisation of major chemical elements in different types of diesel particulate matter collected from in-use diesel engine passenger vehicles, analysed by laser-induced breakdown spectroscopy have been studied by Viskup et al. [26].

The aim of this research is to investigate the minor chemical elements contained in the particulate matter exhaust emissions, generated from diesel engine passenger vehicles equipped with internal combustion engines. For this purpose, we apply high-resolution optical emission spectroscopy technique for precise spectrochemical analysis of DPM. By means of the laser-induced breakdown spectroscopy analytical method, we analyse PM from different on-road diesel engine vehicles. DPM were obtained from miscellaneous in-use diesel engine passenger vehicles of diverse types and models from major brand car producers in Europe.

2. Methodology

Laser-induced breakdown spectroscopy (LIBS) [27–29] is an optical measurement technique [30] for rapid qualitative [31] and sensitive quantitative [32] compositional analysis of various forms of materials like solids [33], liquids [34], gases [35], powders [36] or nanoparticles [37].

In laser-induced breakdown spectroscopy, a high-power laser radiation, with nanosecond or shorter pulse duration, is interacting with the investigating material [38]. This short light-matter interaction generates a plasma, of which the optical emission spectrum is collected by the optical spectrometer and then further processed by computer. From LIBS spectra, the elemental chemical composition of the examined sample can be obtained. The qualitative spectral information can be further calibrated, to obtain quantitative results. The LIBS technique provides very sensitive and rapid analytical measurements, without sample pre-treatment, in the range of ppm levels [39], almost instantaneously. This advantage pushes the LIBS technique forward in many new research areas and makes it also attractive for industrial applications [40].

The LIBS technique can almost instantly measure the minor compounds of DPM and provide the qualitative results about the chemical composition. The fingerprints of minor chemical elements in PM exhaust emissions are related to different processes. These are fuel oil type, fuel quality, fuel composition, fuel additives, engine lubricants, performance of combustion engine, catalytic reaction, particulate filtering technique, deterioration of engine or some parts, etc.

3. Experimental setup

3.1 Experimental LIBS setup

The experimental setup for LIBS measurement consists of high-intensity pulsed laser system, experimental chamber, collection optics and with high precision

optical spectrometer. Laser beam is guided via optical mirrors into the focusing lens. Plasma is generated by focusing of laser radiation into the material. Schema of LIBS experimental set-up is shown in **Figure 1**.

For laser-induced plasma, we have used solid state Nd:YAG laser from Quantel. The laser has 8.5 ns pulse duration, and fundamental laser wavelength operating at 1064 nm in invisible infrared spectrum. For the measurements, we have used the laser energy of 300 mJ per single pulse. Due to the large variations of different DPM samples, we apply higher laser energy, to enhance the plasma emission and to ensure the gain in overall optical signal for all spectra lines and samples. The laser radiation has been focused with 10 cm focusing lens into the plane solid target surface to create plasma. Optical emission from plasma has been collected perpendicularly via optical telescope into the high resolution Echelle spectrograph model Aryelle Butterfly from LTB Berlin equipped with ICCD detector. Spectrometer consists of two separate spectrographs, one part for UV range from 190 to 440 nm and the second part for VIS optical spectrum in range 440–800 nm. Spectral resolution capability is from 3 to 7 pm for VUV part and 4–8 pm for VIS part, thus providing spectral information of a broad spectral range with high resolution and variability. The delay time 1 μs and gate width 2 μs after the trigger signal has been used. The LIBS emission has been recorded in open air atmosphere under an atmospheric pressure at room temperature.

3.2 Particulate matter collection and sample preparation

Sixty-seven different samples from in-use diesel engine passenger vehicles of major brand car producers in Europe have been analysed by LIBS. Vehicles selected for the DPM sample collection were from our daily life environment, as anyone is using to drive to work, etc. Generally, neither special test vehicles, nor driving test cycles or test engines were used. Diesel particulate matter was collected and extracted directly from the tail pipe at the end of the exhaust system. We analysed particulate matter (PM) extracted from the exhaust tail pipe, from 67 different passenger vehicles. Selections of the vehicles were performed randomly and no company, brand or vehicle type was given preference. The collected DPM from Diesel engine vehicles tail pipe deposits has been mechanically pressed into small pellets with 6 mm diameter and with a flat, disc-like shape.

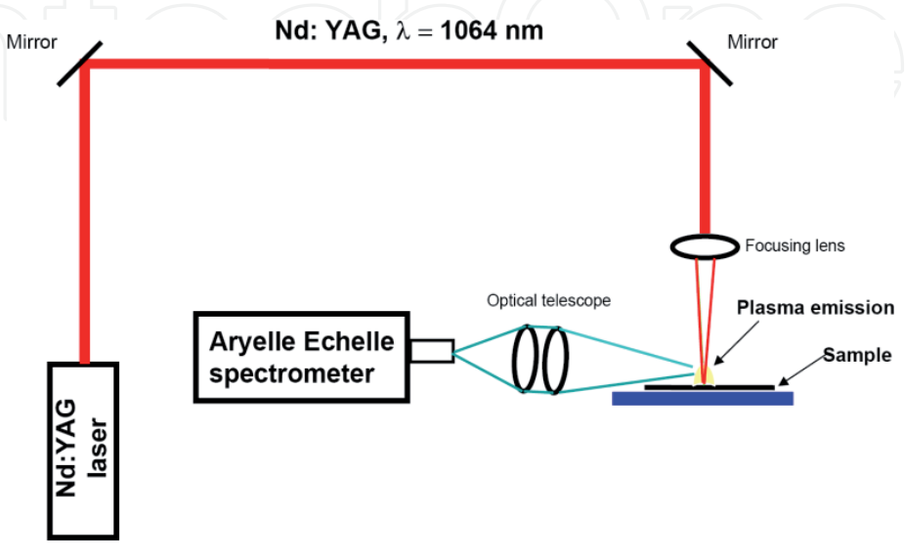


Figure 1.
Layout of LIBS experimental setup.

We are well aware, that it is uncommon to use tail pipe deposits for exhaust particulate matter analysis. It is also worth noting, that the actual composition of this material may differ largely from the particulate matter, which leaves the exhaust system together with the gases. The reason, why we chose to use deposit material is of purely practical nature: As our main goal in this project was to establish the LIBS method for Diesel PM trace element analysis, we needed large sample volumes for many repetitive measurements and the samples needed to provide a shelf life over the entire project time frame. Therefore, this study is not meant to provide representative composition data for airborne particulate matter, but rather to present a methodological approach, that can easily be applied to airborne DPM composition analysis. However, one can still expect to find significant differences amongst individual samples, which arise from the many factors, some of which were enumerated above. Thus, this method of sample collection can be considered sufficient for the declared goal of the project.

4. Results and discussion

4.1 Identification of the major elements in the DPM

Obtained signal from laser-induced breakdown spectroscopy measurements of diesel particulate matter from three selected samples are shown in **Figure 2**. The strong optical emission is characterised from Carbon, Iron, Magnesium, Aluminium, Chromium, Zinc, Sodium and Calcium. These elements were previously identified in PM as major components of diesel particulate matter [26]. LIBS spectra generated from particulate matter collected from in-use diesel engine passenger vehicles exhibits characteristic spikes – optical emission lines with distinct peaks of atomic, ionic and molecular origin included in the signal.

4.2 Identification of the minor elements in the DPM

To identify the minor elements of DPM, the state-of-the-art laboratory laser-induced breakdown spectroscopy setup has been used to obtain high-resolution optical emission spectral images. Here, we restrict our attention to minor chemical elements, particularly to dominant spectral lines from atomic and ionic emission from: Silicon, Nickel, Titan, Potassium, Strontium and Molybdenum.

Minor elements of DPM matrices:

Silicon spectral line: atomic emission from Si I @ 288.16 nm is shown in **Figure 3a**. In this figure, the raw spectral signal from LIBS measurements of 67 different samples of diesel particulate matter is shown. From these spectroscopical results, one can observe that the silicon signal, mainly peak shape, peak intensity and peak width at FWHM varies for each DPM sample. The strength of the LIBS signal of particular atomic or ionic line is basically proportional to the concentration of the analyte in studied sample. Therefore, for detail comparison, we numerically calculated the integral values of each signal peak to obtain qualitative information about chemical composition of diesel particulate matter. The results from these calculations are shown in **Figure 3b**. Here, one can easily compare the variations of silicon signal/concentrations (a.u.) within diverse DPM matrices. However, for detail quantitative analytical characterisation of Si in DPM, the calibration of LIBS signal would be desirable. To compare, very high content of Si is in the sample # 25, 31, 51, 55. From LIBS analytical measurements and numerical

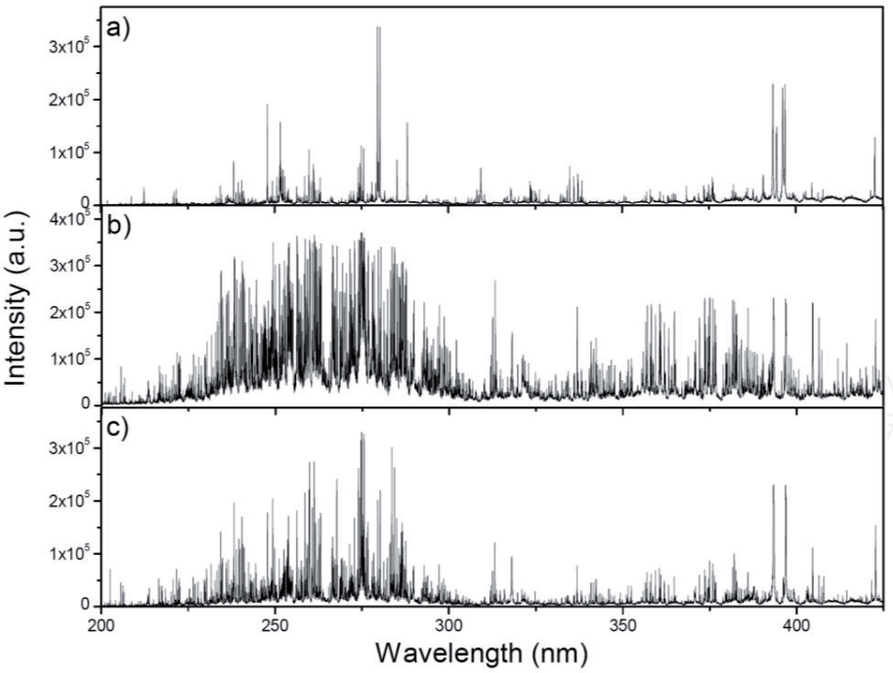


Figure 2.
Optical emission LIBS spectra from three different particulate matter matrices. High intensity spectral lines are from major chemical elements - carbon, iron, magnesium, aluminium, chromium, zinc, sodium and calcium. (a) C, Mg, Ca and Al; (b) Fe, Cr and Ca, Mg; and (c) C, Ca, and Mg.

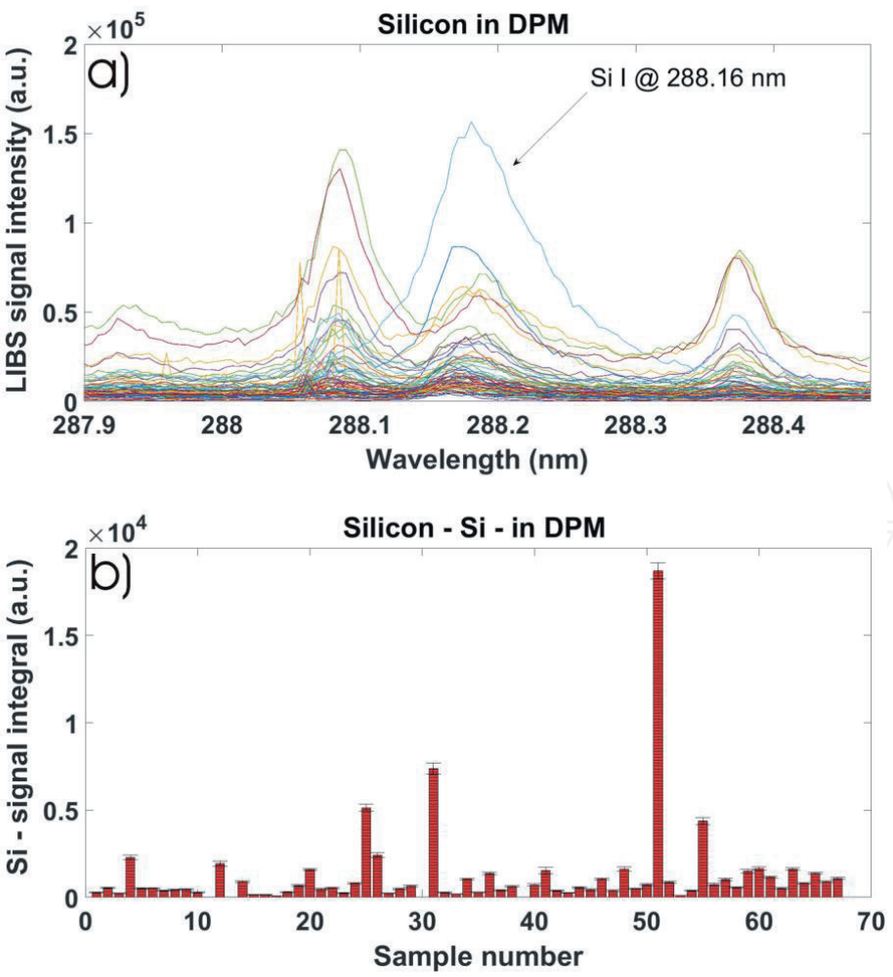


Figure 3.
(a) Optical emission spectra from silicon measured by high resolution LIBS technique from 67 different diesel particulate matter samples collected from in-use passenger diesel engine vehicles. (b) Calculated integral values from Si peak optical emission spectra.

calculations, we can conclude that silicon is minor element and it has been measured in 63 from 67 different DPM samples.

Nickel spectral line: in **Figure 4a**, the comparisons of ionic emission from Nickel, spectra line Ni II at 221.64 nm are shown. One can see that this signal response is quite strong. The results from calculation of peak signal integral values are shown in **Figure 4b**. Samples with high content of Nickel are # 4, 5, 12, 20 and 34. Nickel in DPM is present as minor element in 43 samples.

Titan spectral line: is compared in **Figure 5a**, where the ionic spectra lines Ti II at 334.94 nm are shown. From the numerical calculation in **Figure 5b**, one can see that optical emission from this element is present in 32 DPM matrices. High content of Titan is present in sample # 51, 55 and 59.

Potassium spectral line: is shown in **Figure 6a**, as atomic line K I at 766.48 nm in infrared spectral range. High content has been measured in sample # 4, 8, 25, 26, 28 and 51. The comparison of integral spectral peak calculated values are shown in **Figure 6b**. Potassium is present in 50 different samples.

Strontium spectral line: the raw peak signal from 67 different DPM samples is shown in **Figure 7a**. The Sr ionic line Sr II at 407.77 nm, is present in visible spectral range. From numerical calculation in **Figure 7b**, the Strontium as minor element has been measured in 35 different DPM samples. Strong signal from Sr is in sample # 4, 5, 41 and 51.

Molybdenum spectral line: atomic emission from Mo I @ 390.29 nm is shown in **Figure 8a**. From this figure, higher content of molybdenum is in five samples, # 12,

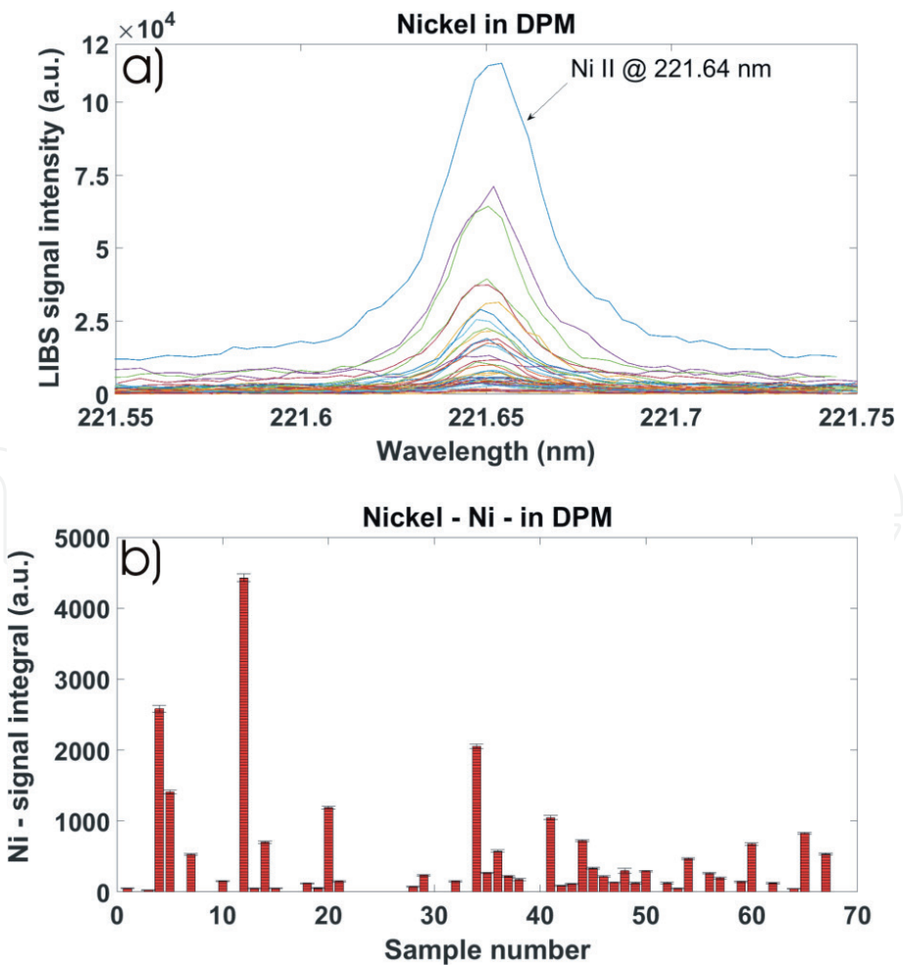


Figure 4.
(a) Optical emission spectra from Nickel measured by high resolution LIBS technique from 67 different diesel particulate matter samples collected from in-use passenger diesel engine vehicles. (b) Calculated integral values from Ni peak optical emission spectra.

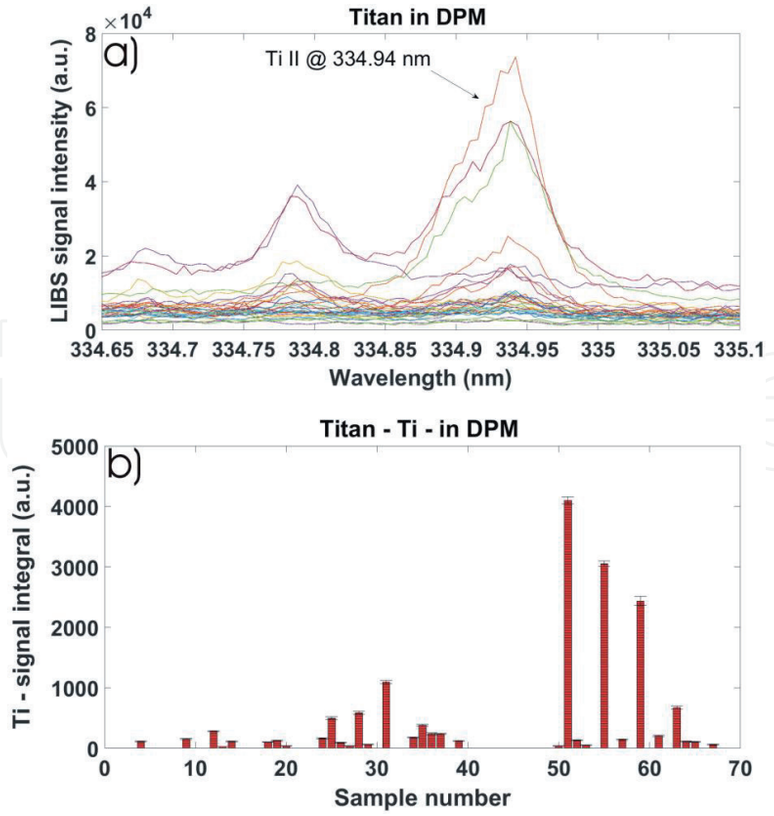


Figure 5.
(a) Optical emission spectra from Titan measured by high resolution LIBS technique from 67 different diesel particulate matter samples collected from in-use passenger diesel engine vehicles. (b) Calculated integral values from Ti peak optical emission spectra.

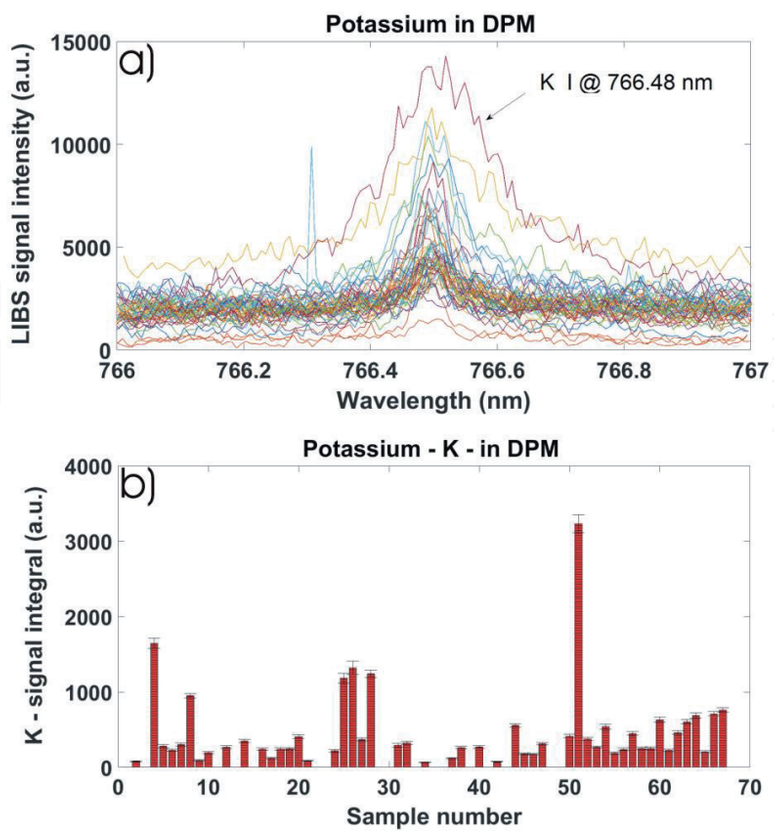


Figure 6.
(a) Optical emission spectra from potassium measured by high resolution LIBS technique from 67 different diesel particulate matter samples collected from in-use passenger diesel engine vehicles. (b) Calculated integral values from K peak optical emission spectra.

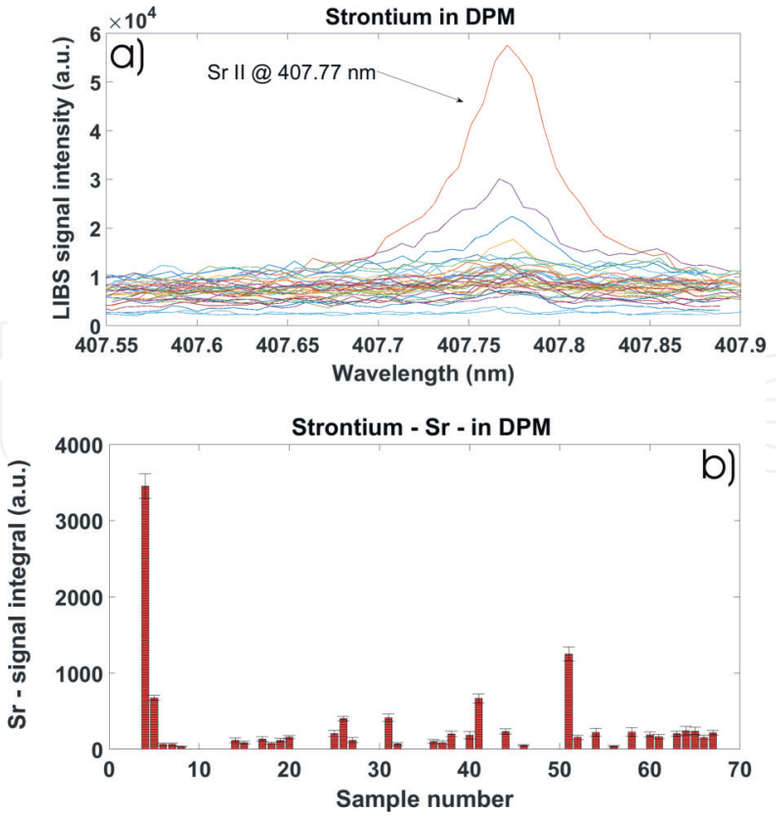


Figure 7.
(a) Optical emission spectra from Strontium measured by high resolution LIBS technique from 67 different diesel particulate matter samples collected from in-use passenger diesel engine vehicles. (b) Calculated integral values from Sr peak optical emission spectra.

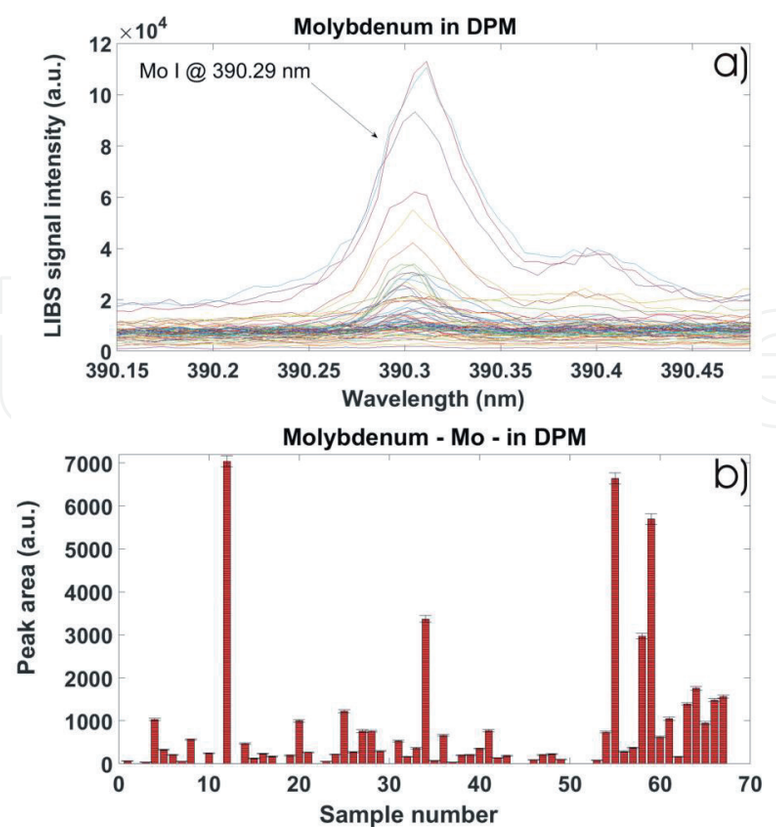


Figure 8.
(a) Optical emission spectra from Molybdenum measured by high resolution LIBS technique from 67 different diesel particulate matter samples collected from in-use passenger diesel engine vehicles. (b) Calculated integral values from Mo peak optical emission spectra.

Analyte	Spectral line	Wavelength (nm)	Detected in/total number of samples
Si	Si I	288.16	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	390.29	55/67

Table 1.
Spectral lines used for analytical measurements and number of samples with detected element.

34, 55, 58 and 59. Molybdenum as minor element has been measured in 55 different DPM samples. The comparison of calculated integral values from Mo peak optical emission spectra is shown in **Figure 8b**.

Table 1 summarised measured analytes, the spectral atomic or ionic lines used for analytical LIBS measurements and number of samples where the minor element has been successfully detected.

5. Conclusions

In this chapter, we have shown an exemplary investigation of the minor chemical elements present in diesel particulate matter. The DPM have been collected from 67 different in-use diesel engine passenger vehicles. Selections of diesel passenger vehicles have been performed randomly, from daily life environment and from major brand car producers in Europe. Particulate matter samples have been analysed spectrochemicaly by means of a high-resolution laser-induced breakdown spectroscopy (LIBS) technique. The qualitative analytical results have shown the presence of minor chemical elements: Silicon, Nickel, Titan, Potassium, Strontium and Molybdenum in diesel particulate matter. These elements were measured by LIBS as strong spectral lines of atomic and ionic emissions in laser induced plasma. The spectral LIBS signal from each minor element was further numerically processed. The integral values of individual signal lines have been calculated to obtain qualitative comparison of individual minor elements in different diesel particulate matter matrices. From analytical measurements and numerical calculations, we can conclude that Silicon as minor element has been detected in 63 from 67 DPM samples. Nickel and potassium have been detected in 43 and 50 samples, respectively. Titan has been detected in 32 and Strontium has been detected in 35 samples of DPM. The element Molybdenum has been detected in 55 DPM samples from different in-use diesel engine passenger vehicles.

Measured minor elements Si, Ni, Ti, K, Sr and Mo together with major elements C, Fe, Mg, Al, Cr, Zn, Na and Ca are forming an important part of the Diesel particulate matter composition. All these elements are altogether contributing to overall exhaust emissions from diesel engine passenger vehicles.

We can conclude that the LIBS technique can almost instantly measure the major and minor compounds of DPM to provide qualitative information about the chemical composition. The presence of these chemical elements in PM exhaust emissions is related to different processes in Diesel combustion engine.

However, in the future, a detailed quantitative analytical characterisation of minor elements, together with a calibration procedure would be necessary to obtain. This would help to understand the minor element concentrations in diesel particulate matter.

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