Chapter

Qualitative Characterisation of Trace Elements in Diesel Particulate Matter from In-Use Diesel Engine Passenger Vehicles by Means of Laser-Induced Breakdown Spectroscopy

Richard Viskup, Christoph Wolf and Werner Baumgartner

Abstract

In this research, we applied laser-plasma spectroscopy technique for the measurement of trace chemical elements in the exhaust emissions generated from in-use diesel engine passenger vehicles. We use high resolution laser-induced breakdown spectroscopy (LIBS) technique for diagnostics of soot and particulate matter (PM). Here we analysed soot and PM, extracted from exhaust manifold part, from different passenger vehicles that are used in daily life environment. The main aim of this study is to reveal the trace chemical elements in different PM matrices. The presence of trace elements in exhaust emissions can originate from different sources: from injected fuel type and fuel additives, engine lubricants, engine combustion process, incomplete catalytic reaction, inefficiency or wear out of PM filtering devices, dysfunctions or failures of engine or vehicle or even information related to polluted intake air.

Keywords: laser-induced breakdown spectroscopy (LIBS), particulate matter, soot, nanoparticles, emissions, emission standards, diesel, diesel engine, diesel vehicles, in-use vehicles, trace elements

1. Introduction

In this research, the laser-induced breakdown spectroscopy (LIBS) technique for diagnostics of trace chemical elements in diesel particulate matter (DPM) formed from in-use diesel engine passenger vehicles has been used [1–3].

Laser-induced breakdown spectroscopy is a powerful spectrochemical measurement technique for fast qualitative and very sensitive quantitative compositional analysis of various forms of matter: solid state, liquid, gas as well as fine powders or nanoparticles [4–6]. One of the pioneers in measurement of particulate trace emissions from vehicles was the group of Schauer et al. [7] 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 [8–11] 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 [12–16] 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 asher digestion procedure for metal determination in biodiesel samples. Different groups used ICP-MS to characterise additional bound elements, such as Cd, As, Ba and Ti in the particulate matter collected from ultra-low-sulphur diesel and biodiesel powered engine exhaust emissions [17].

In the past two decades, a new laser technology evolved in the application of laser-induced breakdown spectroscopy into combustion diagnostics. One of the first research papers that reported the LIBS for on-line engine equivalence ratio measurement was performed by the group of Ferioli et al. [18], followed by research related to measurements of hydrocarbons using LIBS [19]. The implementation of LIBS for in-cylinder measurements was made by Joshi et al. [20], followed by Groß et al. [21]. Another group has studied the LIBS to monitor local lambda values during mixture formation in a direct-injection engine [22]. Different application of LIBS to an engine valve has been used by the group of Lopez-Quintas et al. [23] for mapping of mechanical specimens. Kiefer et al. [24] have used laser-induced breakdown spectroscopy in a partially premixed turbulent jet flame, and the group of Hsu et al. [25] performed measurements of fuel air-ratio in methane-air flames at different pressures. The qualitative and quantitative characterisation of major chemical elements bound in different types of diesel particulate matter measured by laser-induced breakdown spectroscopy technique has been studied by Viskup et al. [26, 27]. And the identification of minor chemical elements in diesel particulate matter by LIBS was studied by Viskup et al. [28].

In this research, the main aim is to measure the trace chemical elements in particulate matter from diesel exhaust emissions. The presence of trace elements in PM can reveal different types of information related to vehicle and engine, combustion process, injected fuel type, fuel additives, engine lubricants, state of selective catalytic reduction devices, inefficiency or wear out of PM filtering devices, engine failure, engine wear out or information related to polluted intake air.

2. Experimental

2.1 Laser-induced breakdown spectroscopy setup

The laser created plasma was generated by the Nd:YAG solid state laser from Quantel corp. This laser operates at the fundamental wavelength of 1064 nm with a pulse duration of 8.5 ns and a laser energy of 300 mJ. The emerged laser radiation has been focused with 10 cm focusing lens into the plane solid target surface to create a 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 sensitive ICCD detector. The spectrometer consists of two separate spectrographs—UV part and VIS part. The UV part is from 190 to 440 nm, and the VIS part of the optical spectrum is from 440 to 800 nm. Spectral resolution is from 3 pm (picometre) to 7 pm for VUV and from 4 pm to 8 pm for VIS part. This Echelle spectrograph provides spectral information in broad range with very high resolution. Optical emission from plasma has been collected

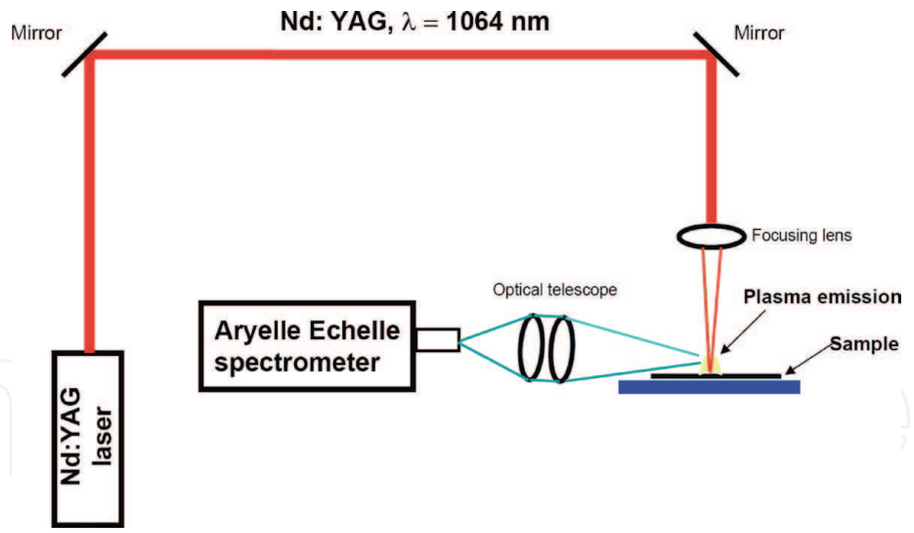

Figure 1.
Layout of laser-induced breakdown spectroscopy setup.

from VUV as well as from VIS parts; thus, the total spectral window from 190 to 800 nm wavelength has been recorded. The delay time of 1 μs after the laser trigger and the gate width of 2 μs were used. The LIBS measurements were performed in open air atmosphere at atmospheric pressure and at room temperature. Layout of the Laser Induced Breakdown Spectroscopy setup is shown in the **Figure 1**.

2.2 Sample preparation and collection

Different PM samples from in-use diesel engine passenger vehicles of major brand car producers in Europe have been analysed by LIBS. Particulate matter has been collected from the tail pipe at the end of the exhaust manifold, while selections of in-use vehicles were performed randomly. Laser-induced breakdown spectroscopy from DPM shows optical emission and spectral lines that are characteristic in ultraviolet and visible spectral region. The collected particulate matter from diesel engine passenger vehicles and exhaust manifold has been mechanically pressed into small pellets with flat disc shape. Each displayed spectrum has been averaged over 12 laser shots.

3. Results and discussion

3.1 Identification of the major chemical elements in PM

Characteristic laser-induced breakdown spectroscopy signal from measurement of diesel particulate matter is shown in **Figure 2**. LIBS spectra generated from particulate matter collected from in-use diesel engine passenger vehicles exhibit characteristic optical emission lines with distinct of atomic, ionic and molecular origin included in the signal. Strong optical emission is from major spectral lines, particularly from carbon, iron, magnesium, aluminium, chromium, zinc, sodium and calcium. These elements were in previous research identified in PM as major components of diesel particulate matter [26].

By means of high-resolution optical emission LIBS spectroscopy, different PM matrices were spectrochemically analysed. From analytical measurements, the composition of major chemical elements in the particulate matter collected from different in-use diesel engine passenger vehicles was obtained. From qualitative

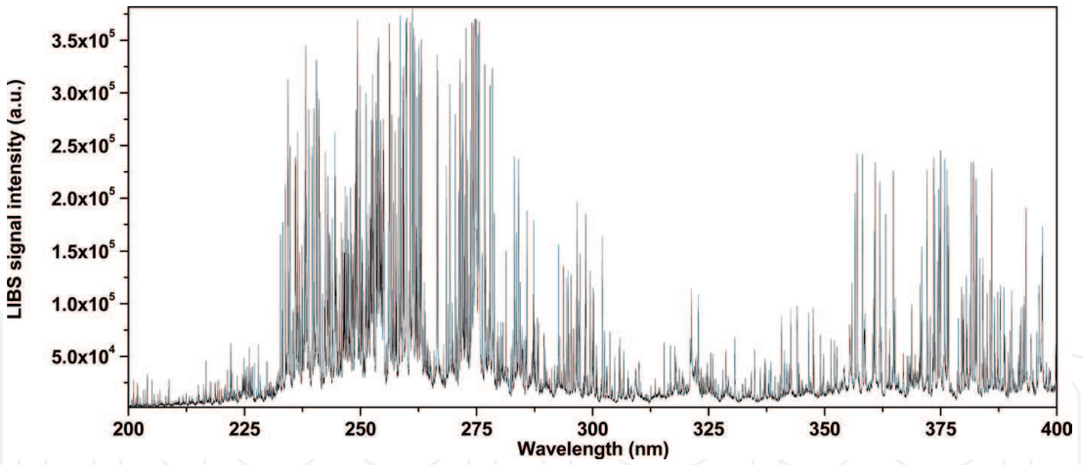

Figure 2.
Optical emission LIBS spectra from diesel particulate matter sample. High intensity spectral lines are from major components carbon, iron, magnesium, aluminium, chromium, zinc, sodium and calcium.

measurements and calibration curves, we found that the major chemical elements of DPM besides the carbon are iron, magnesium, aluminium, chromium, zinc, sodium and calcium with different concentrations. By using quantitative analytical LIBS approach, the maximum concentrations of major chemical elements in DPM from in-use Diesel engine passenger vehicles were measured as follows: Carbon up to ~ 64 weight percent (wt%), Fe ~ 54 wt%, Mg ~ 7 wt%, Al ~ 6 wt%, Cr ~ 6 wt%, Zn ~ 7 wt%, Na ~ 11 wt%, Ca ~13 wt%, for more details see Ref. [26, 27].

3.2 Identification of the minor chemical elements in PM

Further research was dedicated to identify the minor chemical elements of DPM. The state-of-the-art laboratory LIBS setup has been used to obtain high-resolution optical emission spectra images. The qualitative measurements and LIBS signal show the minor chemical elements with optical emission spectra from silicon, nickel, titan, potassium, strontium and molybdenum. More detail study of this topic is presented in Ref. [28].

3.3 Identification of the trace elements in PM

To identify the trace elements in various DPM matrices, the LIBS setup was optimised for optical detection to obtain high-quality spectral data. Acquired signals show optical emissions from trace elements, particularly from barium, boron, cobalt, copper, phosphorus, manganese and platinum in high resolution and in good signal-to-noise ratio. Optical emission spectra from atomic and ionic lines of identified trace elements are shown in **Figure 3**. Here we only select few samples with most pronounced signal to clearly visualise the peak line shape of spectral information.

3.4 Trace elements of diesel particulate matter

Barium spectral line: ionic emission from Ba II @ 455.40 nm is shown in **Figure 3(a)**. In this figure, a raw spectral data from LIBS measurements are shown. Here we select six different diesel particulate matter samples with most intense Barium peak. Selected samples with barium ionic line are samples with numbers 61, 4, 51, 26, 41 and 60. Barium signal has been measured in 26 samples, from 67 different DPM samples, see **Figure 4(a)**. From LIBS spectra, one can observe that analysed signal mainly line peak shape, line peak intensity and line peak width is

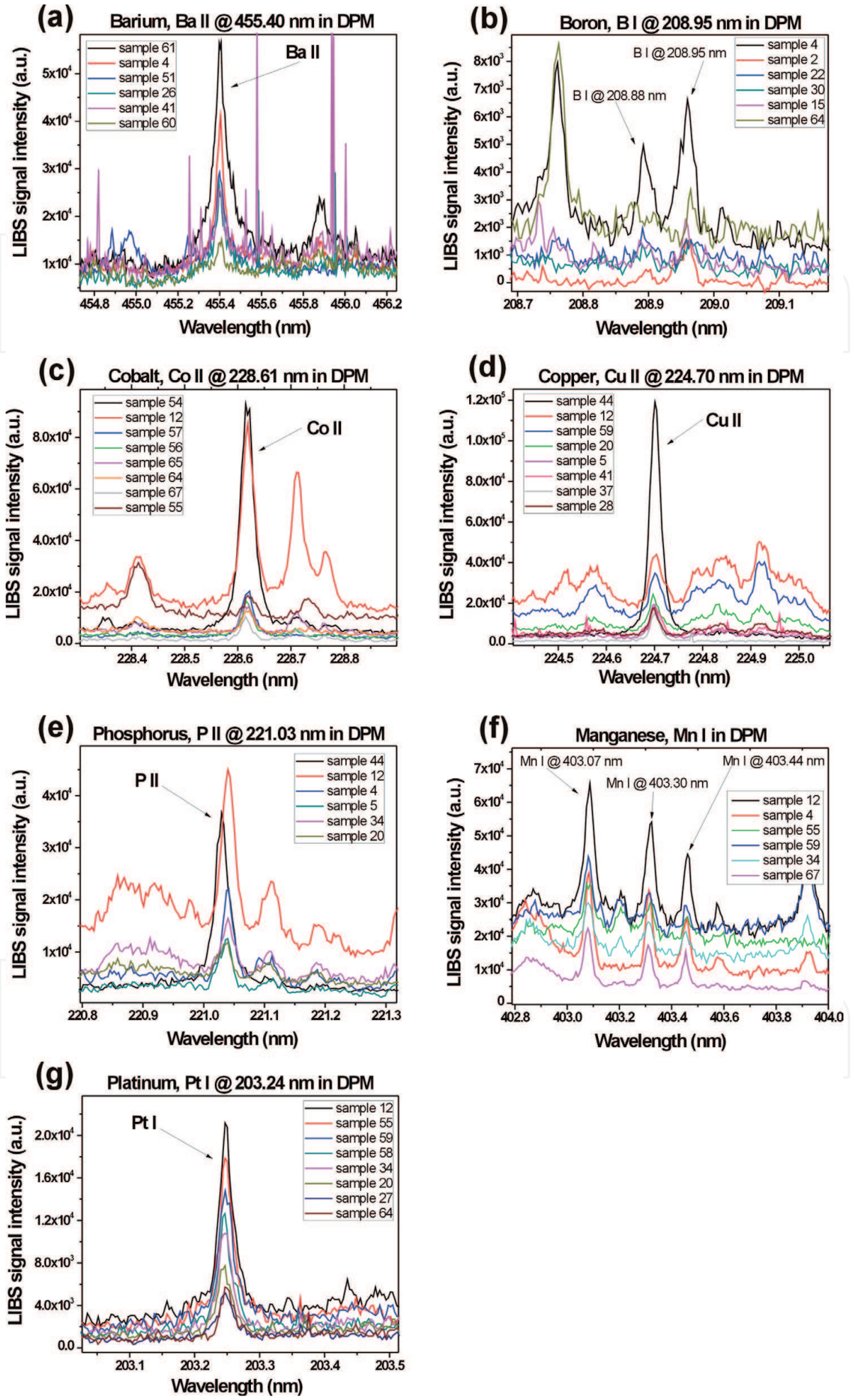

Figure 3.
Optical emission spectra from barium (a), boron (b), cobalt (c), copper (d), phosphorus (e), manganese (f) and platinum (g), measured by high-resolution LIBS technique from diesel particulate matter collected from in-use passenger diesel engine vehicles.

changing according to different DPM samples. The strength of particular atomic or ionic line is basically proportional to the concentration of the element in the studied material. Thus, for qualitative comparison, we numerically calculate the respond signal—the integral of peak values for each spectral line of interest—to obtain information about elemental atomic composition of different types of diesel particulate matter. The results from numerical calculation and integration of peak area are shown in **Figure 4**. From this figure, one can easily compare the individual changes in trace signal related to concentration values in a.u. (arbitrary unit). Nevertheless, in case of exact quantitative characterisation of the trace element in DPM, the particular calibration of trace element signal would be necessary to perform. However, from previous analytical LIBS measurements and qualitative

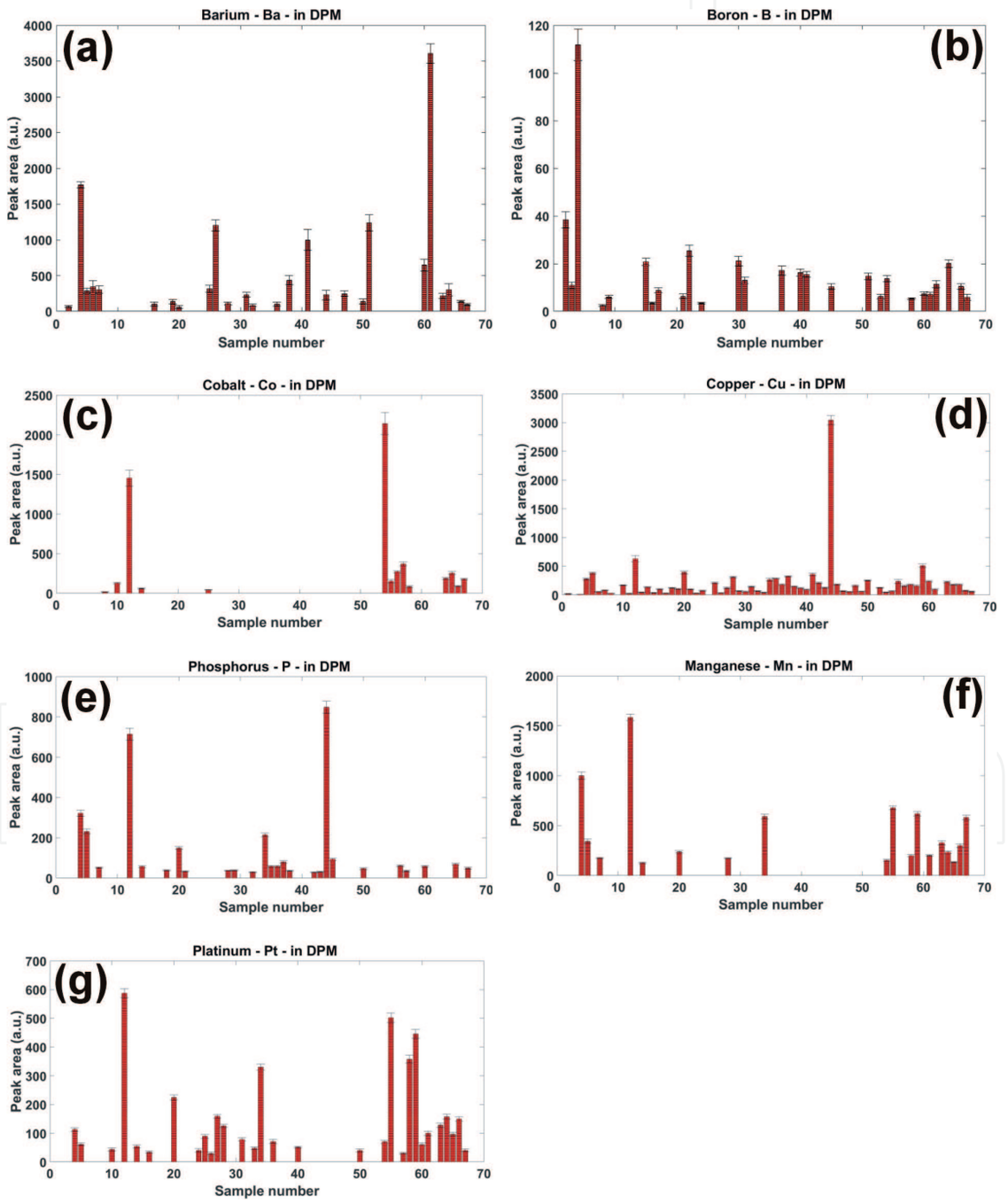

Figure 4.
Comparison of calculated integral values from LIBS optical emission spectra of barium (a), boron (b), cobalt (c), copper (d), phosphorus (e), manganese (f) and platinum (g) trace elements in diesel particulate matter, collected from different in-use passenger diesel engine vehicles.

comparison of LIBS signal of major and minor elements in DPM, we could classify the Barium as a trace element in DPM.

Boron spectral line: in **Figure 3(b)**, measured atomic emission from boron, doublet spectra line B I @ 208.88 nm and B I @ 208.95 nm, is shown. Here we selected six different samples with line emission from boron, where the LIBS signal is clearly visible. The comparison of calculated integral peak values is shown in **Figure 4(b)**. Samples with high content of boron are 4, 2, 22, 30, 15 and 64. Boron is in DPM present as trace element in 27 different samples.

Cobalt spectral line: optical emission from Co II @ 228.61 nm is shown in **Figure 3(c)**. Here, the relatively higher content of cobalt was measured in samples 54, 12, 57, 56, 65, 64, 67 and 55. From numerical calculation of Co II spectral line, signal from cobalt emission was measured in 14 different DPM matrices, as shown in **Figure 4(c)**.

Copper spectral line: this is shown in **Figure 3(d)** as ionic Cu II @ 224.70 nm in ultraviolet spectral range. High content has been measured in samples 44, 12, 59, 20, 5, 41, 37 and 28. The comparison of integral spectral peak calculated values is shown in **Figure 4(d)**. Copper is present in 62 different samples.

Phosphorus spectral line: phosphorus spectral signal from six DPM samples is shown in **Figure 3(e)**. The observed phosphorus ionic line P II @ 221.03 nm is present in UV spectral range. The compared results from numerical calculation of integral peak values are shown in **Figure 4(e)**. Phosphorus trace element has been measured in 26 different DPM samples. Strong LIBS signal from phosphorus element is in samples 44, 12, 4, 5, 34 and 20.

Manganese spectral line: atomic emission from manganese triplet Mn I @ 403.07 nm, Mn I @ 403.30 nm and Mn I @ 403.44 nm is shown in **Figure 3(f)**. From this figure, one can observe higher content of manganese in samples 12, 4, 55, 59, 34 and 67. Manganese trace element has been measured in 18 different DPM samples, and the comparison of integral values is shown in **Figure 4(f)**.

Platinum spectral line: atomic emission from platinum chemical element is shown in **Figure 3(g)**. Here, the spectral line Pt I @ 203.24 nm from eight different DPM samples is clearly visible. Platinum as the trace element was measured in 30 different samples. While most of the intense signal was recorded from samples 12, 55, 59, 58, 34, 20, 27 and 64. Compared integral values are calculated and shown in **Figure 4(g)**.

Analyte	Spectral line	Wavelength (nm)	Detected in/ total number of samples	Most pronounced signal in samples	Chemical element
Ba	Ba II	455.40	26/67	61, 4, 51, 26, 41, 60	Barium
B	B I	208.95	27/67	4, 2, 22, 30, 15, 64	Boron
Co	Co II	228.61	14/67	54, 12, 57, 56, 65, 64, 67, 55	Cobalt
Cu	Cu II	224.70	62/67	44, 12, 59, 20, 5, 41, 37, 28	Copper
P	P II	221.03	26/67	44, 12, 4, 5,34, 20	Phosphorus
Mn	Mn I	403.07	18/67	12, 4, 55, 59, 34, 67	Manganese
Pt	Pt I	203.24	30/67	12, 55, 59, 58, 34, 20, 27, 64	Platinum

Table 1.
Summary of detected trace elements and spectral lines. Number of samples with detected trace signal and samples with most pronounced signal.

In **Table 1,** chemical elements (analyte), spectral lines, number of samples with detected trace element and most pronounced signal from trace element in particular sample number are summarised and investigated.

4. Conclusions

In this research, we have investigated the trace chemical elements contained in diesel particulate matter. The particulate matter has been collected from in-use diesel engine passenger vehicles randomly from different vehicles models. Particulate matter has been analysed spectrochemically by means of a high resolution laser-induced breakdown spectroscopy (LIBS). The qualitative LIBS measurements reveal the presence of trace chemical elements such as barium, boron, cobalt, copper, phosphorus, manganese and platinum in diesel particulate matter. These trace elements were observed as optical emission of atomic or ionic spectral line emission in laser produced plasma. The spectral signal from each trace element was further numerically calculated as integral value of peak width line to obtain qualitative results. From LIBS analytical measurements and calculated signal profile, we can summarise that barium has been detected in 26 from 67 samples. Traces of boron have been detected in 27 samples, cobalt in 14 samples, copper in 62 samples, phosphorus in 26 samples, manganese in 18 different samples and platinum in 30 from 67 DPM samples.

From our previous research, we found out that minor chemical elements in diesel particulate matter are Si, Ni, Ti, K, Sr and Mo [28]. While major chemical elements C, Fe, Mg, Al, Cr, Zn, Na, Ca, O and H are forming the most important part of diesel particulate matter composition [26, 27].

All these major, minor and trace chemical elements contained in particulate matter are contributing to overall exhaust emission composition from in-use diesel engine passenger vehicles.

Finally, we can conclude that the laser-induced breakdown spectroscopy technique is very powerful method for qualitative and quantitative characterisation of DPM. It can almost instantly measure the major, minor and trace components of DPM and thus provide high resolution spectrochemical information about the chemical composition of diverse particulate matter matrices.

The presence of detected major, minor and trace chemical elements in DPM exhaust emissions from in-use diesel engine passenger vehicles can be related to the different processes. Those are: engine combustion process itself, engine health state, dysfunctions of some exhaust filtering device components, etc. These are linked with injected fuel type, fuel additives, engine lubricants, engine wear out, state of selective catalytic reduction devices, insufficient soot or PM filtering devices, engine conditions and quality of intake air.

Nevertheless, in the future, the quantitative characterisation of trace elements and calibration procedure would be an advantage for precise monitoring of different trace concentrations. That would help to better understand the trace content in diesel particulate matter.

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