IDENTIFICATION OF THE MINOR CHEMICAL ELEMENTS IN THE EXHAUST EMISSIONS FROM DIESEL ENGINE VEHICLES

Dr. Richard Viskup, M.Sc. Christoph Wolf, Prof. Dr. Werner Baumgartner
Institute of Biomedical Mechatronics – Johannes Kepler University Linz
Altenberger str. 69, 4040 Linz, Austria
Richard.Viskup@jku.at

Abstract: In this research we investigate the minor chemical elements contain in the particulate matter (PM) exhaust emissions, generated from in - use light duty Diesel combustion engine vehicles. For this purpose we apply high resolution optical emission spectroscopy technique, for precise spectrochemical analysis of Diesel particulate matter (DPM). By means of 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.

Keywords: BLACK CARBON, DIESEL ENGINE, DIESEL EMISSIONS, PARTICULATE MATTER, SOOT, DIESEL VEHICLES

1. Introduction

The existing emission standards like Euro, Tier, or LEV, for light-duty 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. On another hand, there are no specific emission standards for additional compounds or chemical elements contained in the exhaust emissions i.e. in exhaust vapour, in Diesel particulate matter (DPM), in particulate matter (PM), in black carbon / carbon black (BC/CB), or in the soot formed by the Diesel combustion engine. Even though, the chemical elements additional to carbonous particles, present a large fraction of the total DPM or soot emission contents.

Generally, exhaust emissions from Diesel engine 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 [1]. 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 [2], composition [3] and solubility [4]. The particles in Diesel exhaust emission consist of particulate matter - Diesel particulate matter. This is further classified, depending on the size of particles to: particulates of an aerodynamic diameter of less than 10 μm, fine particles of diameters between 2.5 μm, ultra fine particles - below 0.1 μm and nanoparticles - characterised by diameters 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 adsorbtion properties mainly from the unburned or incompletely burned Diesel, particles or from crankcase oil volatilized metallic nano-particles from the cylinder walls.

The aim of this research is to investigate the minor chemical elements contained in the particulate matter exhaust emissions, generated from standard in - use light duty Diesel combustion engine vehicles. For this purpose we apply high resolution optical emission spectroscopy technique for precise spectrochemical analysis of DPM. By means of 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


In Laser Induced Breakdown Spectroscopy a high power laser radiation, with nanosecond or shorter pulse duration, is interacting with the investigating material [16]. 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 [17], almost instantaneously. This advantage pushes the LIBS technique forward in many new research areas and makes it also attractive for industrial applications [18].

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 quality, fuel composition, additives, performance of combustion, catalytic reaction, particulate filtering technique, or wearing of the Diesel engine.

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 Fig. 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 300µJ per single pulse. Due to the large variations of different DPM samples, we apply higher laser energy, to enhance the plasma emission and 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 spectographs, one part for UV range from 190 nm to 440 nm and the second part for VIS optical spectrum in range 440 nm to 800 nm. Spectral resolution capability is from 3 - 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 1µs and gate width 2 µs after the trigger signal has been used. The LIBS emission has been recorded in open air atmosphere under a 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, no special driving test cycles vehicles or collection were from our daily life environment, as anyone is using. Diesel Particulate Matter has been collected and extracted from the tail pipe at the end of the exhaust manifold, after the Diesel Particulate Filter (DPF), if it was applied. Selections of engines were used. Diesel Particulate Matter has been collected and extracted from the tail pipe at the end of the exhaust manifold, after the Diesel Particulate Filter (DPF), if it was applied. Selections of passenger vehicles of major brand car producers in Europe have been performed randomly and no company was given preference. The collected DPM from Diesel engine vehicles exhaust has been mechanically pressed into the small pellets with 6mm diameter and with flat disc shape.

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 the Fig. 2. The strong optical emission is characterise from Carbon, Iron, Magnesium, Aluminium, Chromium, Zinc, Sodium and Calcium. These elements were previously identified in PM as major components of Diesel Particulate Matter [19].

LIBS spectra generated from particulate matter collected from in-used Diesel engine light-duty vehicles exhibits a characteristic spikes - optical emissions lines with distinct 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 spectra image. The qualitative LIBS results of these measurements are shown in Fig. 3(a-f). Obtained signal from minor chemical elements are characterised by strong optical emissions from: a) Silicon, b) Nickel, c) Titan, d) Potassium, e) Strontium and f) Molybdenum.

Minor elements of DPM matrices:

 Silicon spectral line: atomic emission from Si I @ 288.15nm is shown in the Fig. 3a. In this figure the raw spectral signal from LIBS measurements of sixty-seven different samples of Diesel particulate matter are shown. From this 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 Fig. 4a. 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 # 51, 31, 25, 55. From LIBS analytical measurements and numerical 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 Fig. 3b the comparisons of ionic emission from Nickel, spectra line Ni II at 221.64nm is shown. One can see, that this signal is quite strong. The calculation of signal integral values is in Fig. 4(b). Samples with high content of Nickel are #12, 4, 34, 5, 20. Nickel in DPM is present as minor element in the 43 samples.

 Titan spectral line: is compared in Figure 3c, where the ionic spectra lines Ti II at 334.94nm is shown. From the numerical calculation in Fig. 4c 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 Fig. 3d, as atomic line K I at 766.48nm in infrared spectral range. High content has been measured in sample #51, 4, 26, 28, 25 and 8. The comparison of integral spectral peak calculated values are shown in Fig. 4d. Potassium is present in 50 different samples.

 Strontium spectral line: the raw peak signal from sixty-seven different DPM samples is shown in Fig. 3e. The Sr ionic line Sr II at 407.77nm, is present in visible spectral range. From numerical calculation in Fig. 4e the Strontium as minor element has been measured in 35 different DPM samples. Strong signal from Sr is in sample #4 and 51.

 Molybdenum spectral line: atomic emission Mo I @ 313.25nm is shown in Fig. 3f. From the figure, higher content of molybdenum is in two samples, #12 and 59. Molybdenum as minor element has been measured in 17 different DPM. The comparison of integral values are shown in Fig. 4f.

In Table 1 are 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.
Fig. 3 Optical emissions spectrum from: a) Silicon, b) Nickel, c) Titan, d) Potassium, e) Strontium and f) Molybdenum signal, measured by high resolution LIBS technique from Diesel particulate matter collected from in-use passenger Diesel engine vehicles.

Fig. 4 Comparison of calculated integral values from optical emissions spectrum of a) Silicon, b) Nickel, c) Titan, d) Potassium, e) Strontium and f) Molybdenum minor chemical elements in Diesel Particulate Matter.
**Table 1: Spectral lines used for analytical measurements and number of samples with detected element.**

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

5. Conclusions

In this paper, we have investigated the minor chemical elements present in Diesel Particulate Matter. The DPM have been collected from sixty-seven 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 have been analysed spectrochemically 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, Sodium, Potassium, Strontium and Molybdenum in Diesel particulate matter. These elements were measured by LIBS as strong spectral lines of atomic and ionic emission 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 in 32 and Strontium in 35 samples of DPM. The Molybdenum element have been detected in 17 DPM samples from different in-use Diesel engine passenger vehicles.

Measured minor elements Si, Ni, Ti, K, Sr, Mo together with major elements C, Fe, Mg, Al, Cr, Zn, Na and Ca are forming important part of 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 are related to different processes in Diesel combustion engine.

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

Acknowledgements

The authors would like to thank to the Austrian Science Fund – FWF (Fonds zur Förderung der wissenschaftlichen Forschung) for providing financial support. Study was funded by the grant number: FWF - P27967.

References


