Detection of tire tread particles using laser-induced breakdown spectroscopy ☆

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ABSTRACT

The objective of this paper is a study of the potential of laser induced breakdown spectroscopy (LIBS) for detection of tire tread particles. Tire tread particles may represent pollutants; simultaneously, it is potentially possible to exploit detection of tire tread particles for identification of optically imperceptible braking tracks at locations of road accidents. The paper describes the general composition of tire treads and selection of an element suitable for detection using the LIBS method. Subsequently, the applicable spectral line is selected considering interferences with lines of elements that might be present together with the detected particles, and optimization of measurement parameters such as incident laser energy, gate delay and gate width is performed. In order to eliminate the matrix effect, measurements were performed using 4 types of tires manufactured by 3 different producers. An adhesive tape was used as a sample carrier. The most suitable adhesive tape was selected from 5 commonly available tapes, on the basis of their respective LIBS spectra. Calibration standards, i.e. an adhesive tape with different area content of tire tread particles, were prepared for the selected tire. A calibration line was created on the basis of the aforementioned calibration standards. The linear section of this line was used for determination of the detection limit value applicable to the selected tire. Considering the insignificant influence of matrix of various types of tires, it is possible to make a simple recalculation of the detection limit value on the basis of zinc content in a specific tire.

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1. Introduction

The ability to detect tire tread particles in real time and in-situ has importance to a number of real world applications. Wide attention was recently dedicated to a tire tread particles as a source of pollution in environment. It was shown that tire treads contain heavy metals such as Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb [1]. Concurrently with the increase of road traffic, the level of environmental pollution increases not only due to exhaust from combustion engines but also in connection with tire tread particles. Tire tread particles are released mainly in connection with vehicle speed changes; to a lesser extent, however, they are released even in the course of continuous driving. The respective particles consequently pollute air, soil and, subsequently, water sources [1–4].

Another possibility of exploitation of fast detection of tire tread particles might pertain to detection of optically imperceptible braking tracks. This thesis is based on the prerequisite that intense braking results in a higher level of abrasion of a tire tread than in the case of standard driving; therefore the average concentration of tire tread particles on a road surface would be statistically higher at places where braking was performed — in comparison with places where braking was not performed. Introduction of modern braking assistance systems (Anti-lock Braking System, Electronic Stability Control) results in low levels of tire sliding during braking, and therefore braking tracks prove to be visually very badly identifiable. This fact significantly impedes analyses of accidents so it is essential to seek methods and procedures of identification of even such braking tracks.

At present there are two different approaches to detection of tire tread particles. One of them is their detection on the basis of identification of polymers. For example, Gueissaz and Massonnet used pyrolysis in combination with gas chromatography and mass spectrometry (Py-GC/MS) [5] for detection of tire tread particles. Another example of a method used for detection of tire tread particles on the basis of typical polymers is, for example, infrared spectrometry (IR) [6].

Another approach exploits detection of extractable organic zinc, which is added to tires in the form of ZnO2 as a vulcanizing agent. This approach was selected by numerous investigators. On the basis of preparation of a sample and methods such as AAS or ICP-OES it is possible to detect extractable organic zinc, which is present solely in tire treads. An overview of methods focused on detection of tire tread particles including the respective references is listed in Table 1.

This paper suggests detection of tire tread particles using the LIBS method, on the basis of zinc identification. The fundamental benefits of this method include its speed and zero requirements as regards preparation of samples. Simultaneously, it is possible to perform an in-situ analysis at a distance of several meters. For an overview of properties of the LIBS method – in comparison with methods mentioned in Table 1 and some other – see [8,9].

The following sections describe the process of optimization of measurement parameters such as incident laser energy, gate width and gate delay with the objective of obtaining the maximum possible signal to noise ratio applicable to the selected zinc spectral line. Furthermore, the detection limit of the selected zinc line is determined for optimum parameters using the created calibration standards. ICP-OES resp. ICP-MS was selected as the reference method used for determination of zinc content in the selected tires.

2. Experimental section

2.1. Physical and instrumental background of the laser-induced breakdown spectroscopy (LIBS) method

LIBS is a quasi non-destructive method based on the principles of atomic emission spectrometry. The scope of fundamental instrumentation for LIBS comprises a pulsed laser, a lens focusing the laser pulse on the sample surface, optics collecting plasma radiation, a wavelength analyzer and a detector. Detailed description of LIBS principle, methodology and instrumentation is plentiful in the literature [8–12]. Here we only summarize the basic principle.

A short laser pulse (from dozens of fs to units of ns) featuring a major irradiance (several $GW \cdot cm^{-2}$) focused on the sample surface heats up, melts, atomizes and ionizes a small amount of the sample. This complex process as a whole leads to creation of radiating micro-plasma featuring a high temperature. Even though ablation of the material continues solely for several nanoseconds, the created plasma is specific for its high electron density (10^{17}–10^{19} cm^{-3}), high temperature (6000–20,000 K) and rate of expansion of approx. 10^6 $cm \cdot s^{-1}$. Radiation of the micro-plasma may be subdivided into two parts — radiation originating from atomic emissions, and thermic and recombination continuum. The first component of the radiation, i.e. emission radiation, is essential for analyses of samples using the LIBS method as it contains chemical "fingerprints" of each element in the vaporized volume of the sample. Therefore, scanning of the plasma is important following elapse of hundreds on nanoseconds from the laser beam shot. Following elapse of this time we can observe sharp emission lines caused by transitions of electrons from higher energy levels to lower ones while continuous emissions caused by braking emissions and recombination

already prove to be negligible. Plasma radiation is, using reception optics and a fiber optic cable, transported to the input of the spectrometer. The obtained spectrum is recorded using a detector (e.g. CCD) and displayed using a computer.

One of the advantages of this method is the possibility of creation of chemical or element maps. The term of "chemical or element map" refers to the spatial arrangement and relative concentrations of individual elements on a heterogeneous sample [13,14]. LIBS is, considering its chemical mapping properties, frequently used and, in principle, it allows – following completion of a spatially differentiated measurement – for creation of two-dimensional chemical maps for all elements included in the sample. Spatial differentiation of this method is limited solely by the size of the ablation crater featuring the size of dozens of μm.

2.2. Applied instrumentation

Fig. 1 shows the experimental LIBS setup available at the Brno University of Technology. The whole setup consists of dual pulse Nd:YAG lasers, an interaction chamber equipped with two reception optic components and a camera used for sampleview, and two spectrometers. However, solely the primary laser LQ 529a (SOLAR) shown on Fig. 1 no. 1 and spectrometer in the Czerny–Turner (Lot Oriel 260I) arrangement were used for the experiments described below. The laser operates on the frequency of 10 Hz and wavelength of 532 nm, with the pulse length of ~10 ns. The laser beam is led, using mirrors, into the interaction chamber perpendicularly to the sample surface and focused on the sample using a glass triplet (focal distance: 32 mm).

The sample was placed on a handling device inside the interaction chamber (Fig. 1 no. 7) and its position and location of analysis were checked using a preview CCD camera (Fig. 1 no. 2). Plasma radiation was collected using a doublet of lenses ($f = 90$ mm) and, using a fiber optic cable (diameter: 1000 μm), it was led to the entrance of the spectrometer (Lot Oriel 260I) in the Czerny–Turner arrangement (Fig. 1 no. 8). An iCCD camera (iStar 734i, ANDOR) was used as a detector.

The gate delay (t_d) and gate width (t_w) were controlled using a pulse generator (DG535, Stanford Research System, US) and special electronics developed in the laboratory of the Brno University of Technology. All the aforementioned devices prove to be computer-controlled. All measurements were performed in ambient atmosphere, with normal atmospheric pressure.

2.3. Samples

2.3.1. Tire tread

Chemical compositions of tire treads prove to differ in the case of various manufacturers; however, in general it may be stated that it is based on natural or synthetic rubber, resp. a combination of them. During the process of vulcanization, other substances such as zinc oxide, sulfur, filling compounds, reinforcing agents, softeners, antioxidants and antiozonants are added into the rubber structure. Types and dosage of individual additives are trade secrets of individual tire manufacturers.

Table 1
Some analytical methods for tire tread particle detection.

Method	Detection approach	Sample preparation	In-situ detection	Reference
AAS	Zn detection	HNO_3 to pH 2, sonicate, filter	No	[1]
XRF	Zn detection	No	Yes	[2]
EDX	Multielem. analysis	No	Yes	[3]
ICP-OES	Zn detection	HNO_3 digestion, microwave digestion	No	[4]
Py-GC/MS	Polymer detection	No	No	[5]
NA	Zn detection	No	No	[6]
IR	Polymer detection	No	No	[7]

AAS = atomic absorption spectrometry; XRF = X-ray fluorescence; ICP-OES = inductively coupled plasma optically emission spectrophotometry; GC–MS = gas chromatography–mass spectrometry; NA = neutron activation; IR = infrared spectrometry.