TIME RESOLVED LASER BREAKDOWN SPECTROSCOPY (TRELIBS): A NEW TECHNIC OF DIAGNOSIS FOR MINERAL ANALYSIS ON DIESEL SOOT.

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Abstract:
Classical analysis employed for the detection of mineral elements present in diesel soot uses an acid solution to dissolve it. Dissolution generates problems of sample pollution, rate of solubilization ... To avoid this problem, a non-destructive analysis method (The TRELIBS or Time Resolved Laser Induced Breakdown Spectroscopy) using a laser beam which produces a thermal plasma at 20 000 K with excited ions, atoms and electrons is presented here. The spectroscopic study from the atomic and ionic emission enables to characterize the mineral composition of the soot sample. This paper presents this technique for diesel soot collected directly on the exhaust of a diesel engine. Only few seconds are necessary to analyze the sample and to obtain a relation between engine parameters and metallic composition of diesel soot.

1- Introduction:
Air pollution including VOC (Volatile Organic compounds), NOx, SOx, PAH (Polycyclic Aromatic Hydrocarbon), particles are due to combustion process. Lubricant, fuel and engine wear provide metallic species present in soot. Particles diameter emitted by diesel engine are able to be lower than 1 μm [1].
2- Particle collection:

![Diagram of particle collection system](image)

**Figure 1:** System for collecting the exhaust particles from the gas phase.

After the stabilization of the engine working parameters such as temperature of the lubricant and gas exhaust, load, torque..., the 47-mm diameter filter is introduced in the filter-holder in order to collect a part of the particles present in the exhaust gas (Figure 1).

3- Particles analysis:

Filter will be solubilized in different solvents in order to extract the organic and mineral elements [2]. For metal detection in particles, the classic analytical methods as well as the Inductive Coupled Plasma (ICP), the Atomic Emission Spectroscopy (AES), the Spectrometry of Flame Atomic Absorption (SAAF)... require an acid dissolution of the sample [1-8]. But, with those techniques, it is not possible to analyze simultaneously Si, P, S or metals in a same sample because different acids are needed for each species (nitric acid for metallic species, fluorhydric acid for Si, ...) [3]. Furthermore, the solubilization efficiency in acid mixture for organo-metallic complex remains unknown for a complex mixture of PAH particles.

For these reasons, a multi-analysis method has been developed, without sample dissolution or preparation. In this respect, the TRELIBS (Time RESolved Laser Induced Breakdown Spectroscopy) allows to operate directly on the filter, without any sample preparation and with a good detection limit of 1 ppm. This method destroys only a few picograms of soot deposited on the filter allowing to use again this filter for other analysis as its organic composition for example.

4- Description of TRELIBS:

Laser Induced Breakdown Spectroscopy (LIBS) is a new technique based on the analysis of the emission spectra from a plasma induced by the laser beam (1064 nm Nd:YAG with a 100 mJ energy during 6 ns and a fluence of 350 GW/cm² for our experiment) focused on a sample material (gas, liquid or solid) with the diameter of 100 μm on the focus point and a depth of 30 nm [9, 10]. The plasma temperature reaches 20,000 K. Thus, the material of the sample is vaporized, decomposed and ionized for a sample surface of around 10⁻⁴ cm². During the early stages of the plasma thermalization, as electrons interact and recombine with ions,
the energy will be released over a broad range of the energy spectrum. These early stages of

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{TRELIBS technique for surface analysis.}
\end{figure}

the plasma glowing are accompanied by an intense "bremsstrahlung" continuum emission, which is gated off by an electronic detection system. After a 4 \(\mu\)s delay for emission spectra detection, the excited states of the cooled plasma can be detected during 20 \(\mu\)s. The plasma emission is collected and transmitted to an optical emission spectroscopic device thanks to an optical fiber. The time resolved spectral analysis of these atomic emissions can yield a fingerprint of the atomic species present in the sample. This experimental setup presented in Figure 2 permits a surface analysis of soot or sootless filters.

In order to control the target position, two motorized computer-controlled linear stages for X-Y movement and a manual micrometer for Z adjustment were used. For all measurements, the target is horizontally displaced between laser shots to allow the sampling from a fresh location. So, the reproducibility of line intensities is obtained by scanning the entire target surface. A software (computer 2 on scheme) was developed to synchronize the motorized stage movements with the laser spot. The plasma emission is collected and transmitted to a 1 meter focal length spectrometer (300 or 1200 grooves/mm) through a quartz optical fiber. One end of the optical fiber without lens coupling is perpendicularly positioned to the laser beam at 5 mm from the plasma plume. At the exit of the spectrometer, a gated image intensifier allows time resolution of plasma emissions with a nanosecond precision in order to eliminate the Bremsstrahlung continuum emissions. For this reason, a delay of 4 \(\mu\)s is needed between the end of the laser pulse and the beginning of spectral acquisition. In order to detect all elements, we scan all the wavelengths by using different gratings (300 or 1200 grooves/mm).

The plasma emission was monitored with an OMA 4 equipped of a CCD matrix detector providing a resolution of 0.016 nm/pixel.

An external trigger from the laser Q-switch was used to synchronize the incident laser pulse with the gate opening. The detector operations are driven by an OMA 4000 (PAR) or a WINSPEC V1.6.2 software.

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5- Filters choice:

![Figure 3: TRELIBS analysis of clean quartz and fluorocarbon filters.](image)

Filters used for particles collection must be chemically inert and do not contain metallic species which are likely to be present in diesel soot such as Mg, Fe, Cu, Zn, Ca. As we can see on figure 3, Quartz fibers filters provided by Pall Gelman are much cleaner that Fluorocarbon coated glass Fiber filters also provided by Pall Gelman, so Quartz filters were preferred in our study.

6- Qualitative analysis of diesel soot by TRELIBS:

Figure 4 shows a spectrum comparison between clean and dusty filter for metals. The difference of emission intensity obtained from these 2 categories of filter allows to identify the specific mineral elements, present in diesel soot: Mg, Fe, Cu, Ca, Zn are the main metallic species contained in diesel soot.

CN lines are important on dusty filter because soot contains essentially carbon species while they have a minor intensity on clean fiber filters. Some authors shows a relation between the nature of carbon atomized and intensity of CN lines. The CN lines represent the nitrogen - carbon reaction in the plasma arc on the target \((C_2 + N_2 \rightarrow 2\ CN)\) [11].

An increase of the pulse on the same area gives us the analysis.

![Figure 4: Emission spectrum of metallic species present in diesel soot.](image)

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from the surface to the bulk of the filter.

7- Quantitative analysis of diesel soot by TRELIBS:

The high sensibility of the TRELIBS method (about 1 ppm) allows us to measure the metallic elements included in the polycyclic aggregates. In order to quantify their evolution with the working parameters of the engine, a semi-quantitative measure was developed by using Si atomic emission as a reference element for every atomic emission [12]. Indeed, on Quartz filter, Si presents characteristic lines in most of studied spectral windows. By using the most intense line of Si, we are able to note the elements observed by TRELIBS in soot and their relative concentration with regard to Si.

In figure 5, are correlated the engine air/fuel ratio to the concentration of the specific metallic species on diesel soot. An important air excess generates little soot.

We will note that filters studied contain the same mass of particles whatever the air/fuel ratio (different sample time). The predominance of carbon lines clearly appears: the intensity of carbon line is about one hundred of the Si line. Furthermore, a correlation exists between carbon species and CN bands intensity [11]. Other mineral species at low concentration, such as Ca are present in diesel soot. It seems that these concentrations decrease with the increase of air/fuel ratio (except for Cu and Zn). In a near future, we expect to be able to correlate the soot composition with the main engine parameters or with the rate of metallic elements of the gas and lubricant.

8-Conclusion:

In this way, the TRELIBS technique allows quasi-instantaneous analysis (few μs), which requires no preparation of sample. By simple comparison of emission lines between a reference clean and sample filter, it is possible to clearly identify all the metals present on diesel soot and to give a spatial distribution of soot particles relative composition. The analysis shows that Fe, Cu, Ca, Zn, Mg are the principal metallic species present in diesel soot on the reference filter.

Finally, TRELIBS appears as a new powerful and convenient method for characterization of mineral elements, carried in an area smaller than 0.01 mm².
