Discriminant Analysis of Coal Samples by Laser Induced Breakdown Spectroscopy

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Abstract
The quick analysis of coal samples is fundamental in many industrial processes to optimize the operation and minimize the pollution emission, for soot is one of the main pollutants generated in coal combustion. LIBS is a technique that has a great potential for real-time analysis of coal and soot samples. In particular, we have investigated here the applicability of LIBS to the discrimination of coal and soot aerosols of different origins.

Introduction
Laser induced breakdown spectroscopy (LIBS) is a modern, versatile atomic spectroscopy technique, which is becoming increasingly popular in recent years both in quantitative and qualitative applications. The advantages of LIBS analysis include that it is fast, needs practically no sample preparation, samples of any size and phase can be analyzed, it is virtually non-destructive, and it can be applied also in the field using compact/portable LIBS devices or remotely [1].

The objective of the present research was to assess the information content of LIBS spectra of bulk carbon samples and of aerosols (soot, carbonaceous aerosols) generated from these coal samples by laser ablation. In particular, the LIBS analysis can potentially reveal the elemental composition (contaminants) of the samples and can be the basis of sample discrimination due to their varying trace element content (coal types and aerosol sources may be classified based on the obtained LIBS spectra). The technique builds on the phenomenon of laser induced breakdown, namely that if the energy density of a pulsed laser beam focused on the sample, an ablation and plasma formation will occur in the focal spot of the beam. The analytical information about the elemental composition of the sample then can be gained from the emission spectroscopic observation of this microplasma.

Different types of coal are extensively used as fuels and industrial raw materials. Combustion of coal is one of the main sources of energy, but it generates ash soot aerosol which is one of the main antropogenous air pollutant. Thus the examination of these samples requires newer and newer chemical and physical techniques [2].

The goals of this research were exploring the chemical and physical attributes that can be measured by the LIBS investigation of carbonaceous samples (graphite, anthracite, lignite and other coal types) and their aerosols. In the present study, six different coal samples, obtained from local depos, were analyzed.

Experimental

The samples studied originated from different locations and have different caloric values. The six samples studied were identified as „Graphite", „Anthracite", „Czech brown coal", „Polish brown coal", „Lignite" and „Pécs-vasasi brown coal".

For the purposes of LIBS measurements, a special, windowed sample cell was fabricated, in which the application of a selected standing or flowing gas environment was also allowed. The samples were machined to a specific shape and size before analysis: disks of 23 mm in diameter and ca. 5 mm in thickness were made and used both in bulk and aerosol measurements. We recorded all spectra in grade 4.5 purity nitrogen.

An Applied Photonics LIBScan 25+ Nd:YAG laser was employed for plasma generation (50 mJ pulse energy, ca. 10 ns pulse length), focusing the laser beam into the cell through the top window. The plasma emission was collected from the side by quartz lenses and 200 µm diameter solarization resistant fiber optic cables and detected by an Avantes AvaSpec FT2048 CCD spectrometer in the 190-880 nm UV-Vis spectral range. The start of the spectral data collection was triggered by a fast photodiode observing the plasma initiated by the laser.

The carbonaceous aerosol was generated in a KrF laser based ablation setup. The laser worked at 248 nm with 18 ns long impulses. The energy density of the focused beam was 2.5 J/cm^2 and the repetition rate was ca. 1 Hz. The concentration of the aerosol generated from graphite was found to be ca. 10^7-10^8 m^{-3} and the mode of particle distribution was at around 150 nm [3].

Discriminant analysis is an upcoming research direction in LIBS spectroscopy. This is due to the realization that LIBS spectra are line-rich and very characteristic ("fingerprint-like) of the sample. In novel, related works, chemometric (statistical) methods are used to discriminate the LIBS spectra of samples, which can be made automatic and the efficiency of recognition can be also raised. The simple chemometric methods are based on calculating a Q similarity index which's value the higher the more the two spectra similar. Q can be defined and calculated in various ways. It is common to count from the linear correlation (LC) of the spectra [4], but the methods based on the sum of squared differences (SSD) and overlapping integral (OI) are also widespread [5]. Advanced chemometric methods can also be employed. For example, our research group ealier successfully used Multivariate Curve Resolution Alternating Least Squares (MCR-ALS), Discriminant Analysis (DA) and Classification Tree (CT) methods to discriminate paper and ink types. In the present study, we also employed these methods, a brief description of which can be found in [6], to discriminate coal sample types.

Results and discussion

The spectra of bulk coal samples contained intensive, characteristic atomic lines (Ca, Na, N, C), but some molecular lines (C$_2$, CN) also appeared. This is illustrated in **Fig 1**. The elemental composition was different at different points of the samples due to inhomogeneity, but the inter-sample differences were found larger than intra-sanple differences.
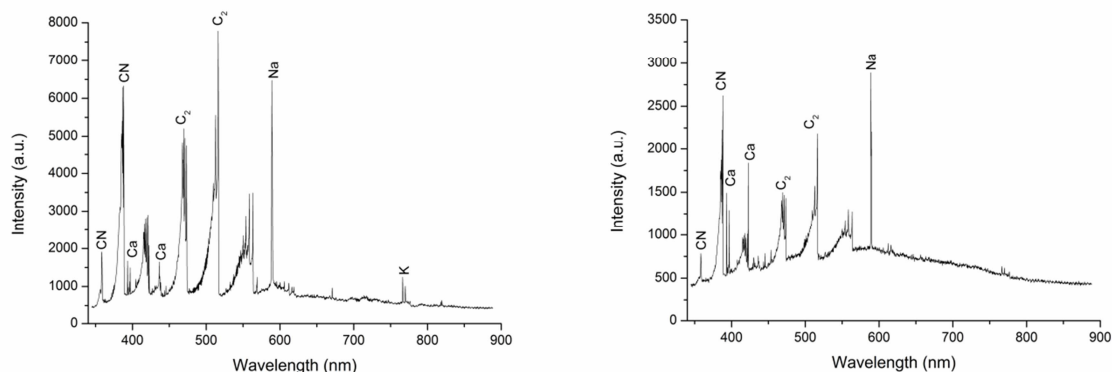
Fig 1. LIBS spectra of the bulk anthracite (left) and Polish brown coal (left) samples

In the case of coal aerosols, not all laser pulses hit a particle during LIBS analysis, therefore a pre-processing of spectral data is needed - only those spectra which contain carbon spectral lines above a certain intensity are retained. We also found that the relative frequency of plasma generation was different for different samples. For example, the relative number of successful shots with "anthracite" aerosol was 2%, whereas it was 80% with lignite. This difference may be explained by different breakdown thresholds or by different particle concentrations. Aerosol spectra collected were also found to be less intensive and had worse peak to noise ratio than those of bulk samples. They were also found to be less characteristic. Two aerosol spectra can be seen in **Fig. 2**.
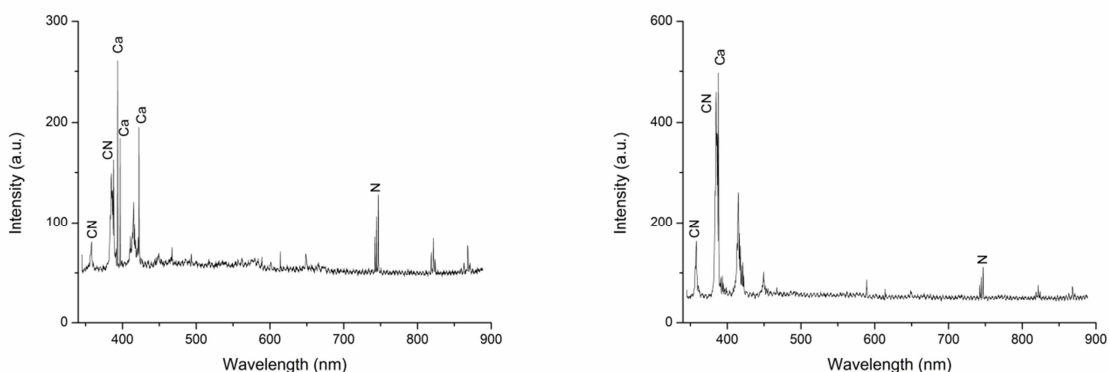

Fig 2. LIBS spectra of anthracite (left) and Polish brown coal (left) aerosol

Due to the above characteristics, the discrimination of bulk coal samples is relatively easy. We successfully identified the samples by all three simple and two advanced statistical methods alluded to above. We found the best discrimination results with the linear correlation method, calculated on the full UV-Vis spectra (**Fig. 3**). The combined MCR-ALS/CT method was also found to be efficient (**Fig. 4.**)
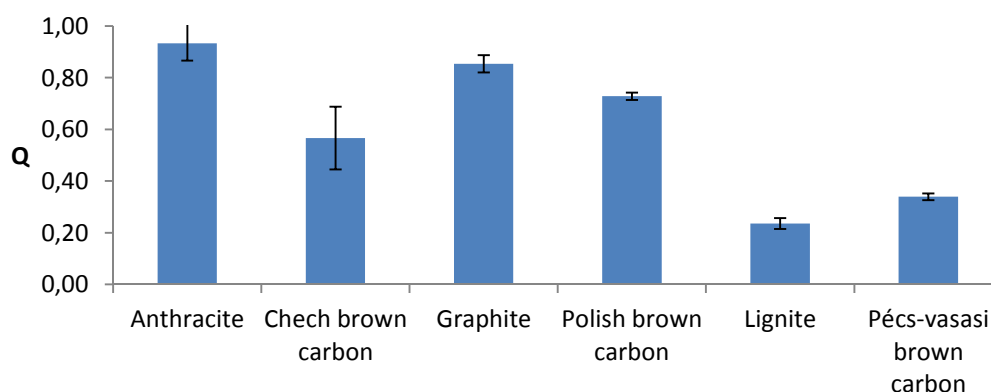
Fig 3. Discrimination results for the LC method, based on UV-Vis spectra and anthracite reference. Q= 1 means complete similarity, whereas Q=1 complete dissimilarity
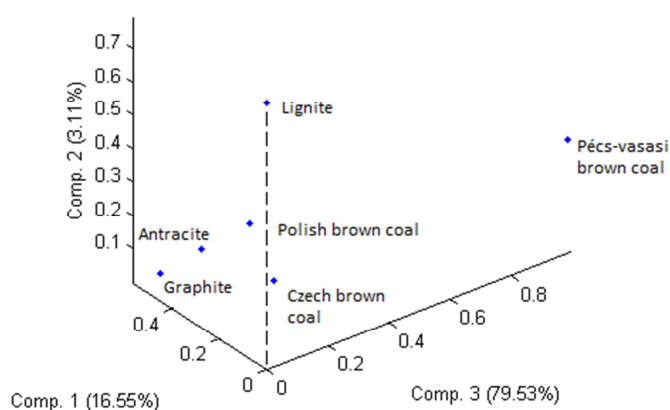

Fig. 4. Discrimination of coal samples according to MCR-ALS method, based on their UV-Vis spectra

We found that simple numerical methods are not capable of sufficiently discriminate different soot aerosol types. This is probably mainly caused by the poor S/N ratio in the spectra, which for this reason, also are highly similar to each other.

On the other hand, more advanced chemometric methods, such as MCR-ALS/CT were found to be powerful enough to efficiently discriminate aerosol spectra. In fact, it was even possible to create a model, which is able to discribe both the bulk and the aerosol samples. The results of the assignation are shown in **Fig. 5.** below.
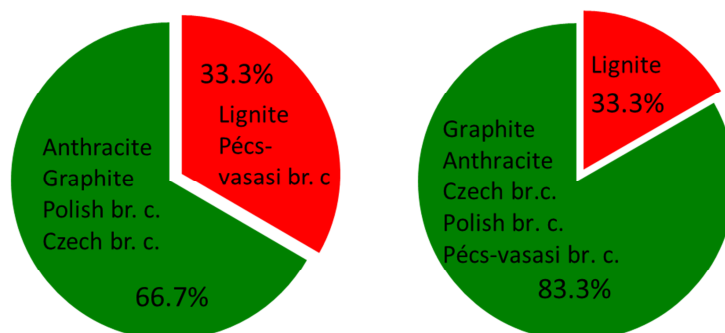
Fig. 5. Results of discrimination of bulk (left) and aerosol (right) samples according to the CT method, and based on visible range spectral data

Conclusion

We successfully created an experimental system, in which we could measure bulk coal and soot aerosol samples by LIBS spectroscopy, in a nitrogen atmosphere. Simple and advanced chemometric techniques were successfully employed to discriminate different bulk coal samples from each other, as well as to identify the source coal type of soot aerosol samples. The aerosol analysis was performed on about aerosols having ca. 10^8 m^{-3} particle concentration and about 150 nm average particle size.

References

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