Qualitative Discrimination Analysis of Coals Based on Their Laser-Induced Breakdown Spectra

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ABSTRACT: Six different coal samples (anthracite, Czech brown coal, Polish brown coal, lignite, graphite, and Pécs-vasas brown coal) were studied by using laser-induced breakdown spectroscopy (LIBS) in order to assess its capability for use in coal quality control. The spectral features of the coals as well as their correlation with the results of proximate analysis was investigated. The second part of the study deals with the classification (qualitative discrimination analysis) of coals based on their visible-range LIBS spectra using various statistical methods. Canonical linear discriminant analysis was found to be the most efficient; using five canonical variables and after reducing the spectra to 18 variables, the achieved classification accuracy was 95.33% according to the cross-validation test of the model. The described results indicate that LIBS data can be efficiently used for the quality control of coals and thus can also contribute to the indirect control of the combustion process.

1. INTRODUCTION

Coal energy continues to generate power for millions of people in coal-fired power stations, and coal quality obviously plays an important role in the process. In order to make it as economical, efficient, and environmentally friendly as possible, the coal quality and the combustion process need to be continuously monitored and controlled. Generally, two approaches can be used. One is precombustion" coal quality analysis, which assesses the coal before it enters the boiler. The other far more often employed one is the postcombustion approach, in which the fly ash produced by the process is investigated. In the latter approach, mainly the unburned carbon content (UC) is measured as it not only provides a feedback on the combustion efficiency but also because high levels of UC adversely impacts the recycling of fly ash, which mainly aims at using it as pozzolan in cement.[1−3] Coal handling and preparation plants also extensively use coal quality monitoring systems.[4] For many years, the monitoring was done via sampling of the coal or ash and performing proximate analysis in laboratories, but modern coal-based plants use online analytical instrumentation for this purpose.[4−7]

Most commercially available online monitoring instruments currently used in power plants work by the microwave absorption, near-infrared spectroscopy, prompt gamma neutron activation analysis, or X-ray fluorescence spectroscopy principle, but other analytical techniques, such as gamma ray scattering, have also been suggested and tested for this purpose. Many of these techniques however have unfavorable characteristics, such as radiation hazard, bulkiness, dependence on grain size, high investment costs, or the necessity for frequent recalibration, and so on.[5,7,8] The recently developed methodology for real-time source apportionment of the combustion generated carbona-

ceous particulate matter combined with field-adopted, robust photoacoustic instrumentation also has a remarkable potenial in this field.[9−11]

One additional promising technique recently proposed by several studies for use in coal quality monitoring is laser-induced breakdown spectroscopy (LIBS).[5] LIBS is an increasingly popular laser atomic spectrometry technique, which is capable of providing elemental composition data (either at the level of trace, minor, or major components) about practically any solid, liquid, or gaseous sample without substantial sample preparation; thus, the analysis is very fast. The instrumentation needed is reasonably simple, very robust, and available in a compact portable format, and stand-off analysis is also possible.[12−14] As a result of these uniquely advantageous set of characteristics, LIBS is more and more used in industrial automation applications,[15] such as coal and fly ash analysis.

The primary analytical objective in this coal-related LIBS application is the determination of the carbon content of coal and fly ash,[5,16] but methods have also been developed for the estimation of the calorific value, volatile content, and ash content[17,18] and for the quantitation of other inorganic components.[19,20] In terms of carbon content analysis, the results univocally indicate that the conventional univariate calibration approach does not provide adequate accuracy. The best quantitative results have been achieved by using multivariate calibration methods, such as partial least-squares[17,21] or linear multivariate regression,[22] combined with spectrum standardization.[23]

The goal of the present study was to assess the capability of LIBS spectroscopy for the qualitative discrimination analysis of different coal types (e.g., anthracite, brown coal, lignite, etc.) by using comparative statistical functions and linear discriminant analysis. The motivation behind this analytical approach is that the online LIBS qualitative analysis of the coal either during mining or while being fed to the power plant on a conveyor belt can provide a substantial contribution to the quality control.

2. EXPERIMENTAL SECTION

2.1. Instruments and Methods. All LIBS measurements were carried out by using a portable LIBS system (LIBScan 25+, Applied Photonics, UK) accessorized with an external fiber-optic CCD spectrometer (AvaSpec-2048FT, Avantes, NL). The Nd:YAG laser was operated in the single-pulse mode, emitting 50 mJ pulses of 4 ns duration at the 1064 nm fundamental wavelength. Light collection was implemented via solarization-resistant 0.22 NA optical fibers (FCB-UV200−2-SR, Avantes, NL) and fused silica collimating lenses (COL-UV/vis, Avantes, NL) set at an about 45° observation angle. Gating of the spectral data collection was achieved by the internal electronics of the spectrometer, which was triggered by the laser power supply unit. The gating signal was continuously monitored on a digital storage oscilloscope (TDS1002, Tektronix, USA). The minimum possible integration time (2 ms) and a gate delay of 1 μs were set at the spectrometer. The double-channel spectrometer allowed the recording of the plasma emission in the spectral ranges of 198−318 nm and 344−888 nm, with resolutions of 0.09 and 0.4 nm, respectively. A three-axes manual translation stage (LT3/M, Thorlabs, USA) was used to bring the samples in focus and to select the area of interest for analysis.

2.2. Samples and Materials. The set of samples used consisted of six coal samples, including both low- and high-rank coals. Five coal samples were obtained from commercial sources in Hungary. These were identified as follows: lignite (L), anthracite (A), Pécs-Vasas brown coal (PV), Polish brown coal (P), and Czech brown coal (C). The graphite (G) sample was of >99.95% purity and was obtained from Goodfellow, UK. The only sample preparation performed prior to LIBS analysis was to cut the samples into a disk shape with 23 mm diameter and 5 mm thickness.

The same samples were also used in other studies in progress in our laboratory; thus, some of their combustion-related properties were also measured.[24] Table 1 lists the moisture, volatile matter, fixed carbon and

Table 1. Results of the Proximate Analysis of the Coal Samples

sample ID	moisture (%)	volatile matter (%)	fixed carbon content (%)	ash content (%)	calorific value (kcal/kg)
anthracite (A)	1.74	7.77	88.59	1.89	7201
Czech brown coal (C)	2.45	53.38	39.88	4.26	6632
Polish brown coal (P)	4.75	35.23	55.53	4.47	6725
lignite (L)	5.74	42.59	19.69	31.96	3540
graphite (G)	1.18	4.93	93.36	0.51	7687
Pécs-Vasas brown coal (PV)	n.a.	15.26	n.a.	41	3300

ash content, and the calorific value of the studied coal samples. Please note that in some countries (e.g., US and Canada), the brown coal designation is not used but is represented by further subcategories, such as bituminous and sub-bitumineus coal, and so forth.

2.3. Data Evaluation. Spectral line assignation was done using the NIST Atomic Spectra Database. Linear discriminant analysis (LDA) was performed in Origin Pro 8.6 (OriginLab, USA), whereas the calculations using comparative statistical functions were executed in MS Office Excel 2010 (Microsoft, USA), also by using Visual Basic for Applications macros. All illustrations were produced in Origin or in Xara Extreme 5 (Xara, UK).

Three comparative functions, namely, linear correlation (LC), sum of squared deviations (SSD), and overlapping integral (OI), were used in the calculations. The use of these functions are well-known but also were described in detail in our earlier qualitative discrimination studies (e.g., refs 25 and 26). In our implementations we normalize these functions to the range of 0−1. This range defines a degree of similarity (Q), where a value of 1 means "full similarity" and $Q = 0$ indicates "full dissimilarity" of the compared spectra. LDA is a well-described multivariate method widely used in statistical analysis and is a so-called supervised linear transformation technique which calculates the variables (discriminants), the use of which as "projection axes" will result in a maximum separation between data classes.[27] In this study, we used the dedicated LDA module in the Origin Pro software. Spectrum normalization, by using the total integrated light in the spectrum as reference value, was also used during the data evaluation. Net intensities were calculated by performing two-side linear background correction.

3. RESULTS AND DISCUSSION

3.1. Spectrum Repeatability. Good spectrum repeatability is a prerequisite of a reliable discrimination analysis. Unfortunately, signal intensities show substantial variation (scatter) in single-pulse LIBS measurements even when homogeneous, pure metallic samples are analyzed; thus, spectrum repeatability is fair at best.[12,13] In case of heterogeneous samples, such as coals, one can expect additional variability between the LIBS spectra taken at various locations of samples. Although the repeatability can potentially be improved by using averaging over a large number of spectra (e.g., as many as 500) taken at various locations on the sample surface, this approach significantly decreases the sample throughput with compact LIBS systems typically capable to perform only a few measurements per second; thus, we first tested the repeatability of the spectra of our samples.

For the purposes of this test, many visible-light (vis) spectra from every sample were compared to each other (for the same sample) by using the LC function. It was found that when the number measurements was increased to about 25, the average degree of similarity (Q) improved to 0.9 or higher with a relative standard deviation of only 5% or less (Figure 1). It was therefore
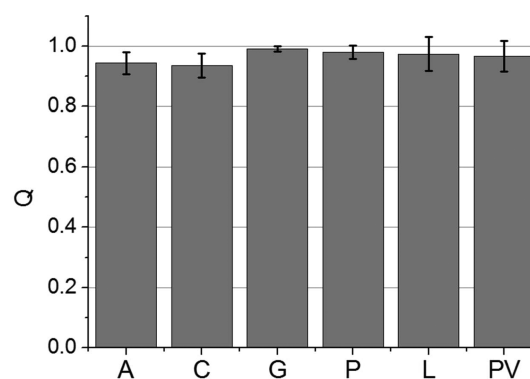
Figure 1. Repeatability of the spectra for each sample, as tested by the LC function on 25 spectra (i.e., 25 spectra taken on different locations on the same sample were compared to each other). $Q = 1$ indicates complete similarity.

concluded that the repeatability is sufficiently good with 25 repeated measurements; thus, in the rest of the study this many observations (spectra) were recorded for each sample.

3.2. Description of the Collected LIBS Spectra. The UV spectra of the samples were found to be relatively uneventful. Only a few spectral lines appear in the spectra, which can be mainly associated with the carbon, magnesium, silicon, and
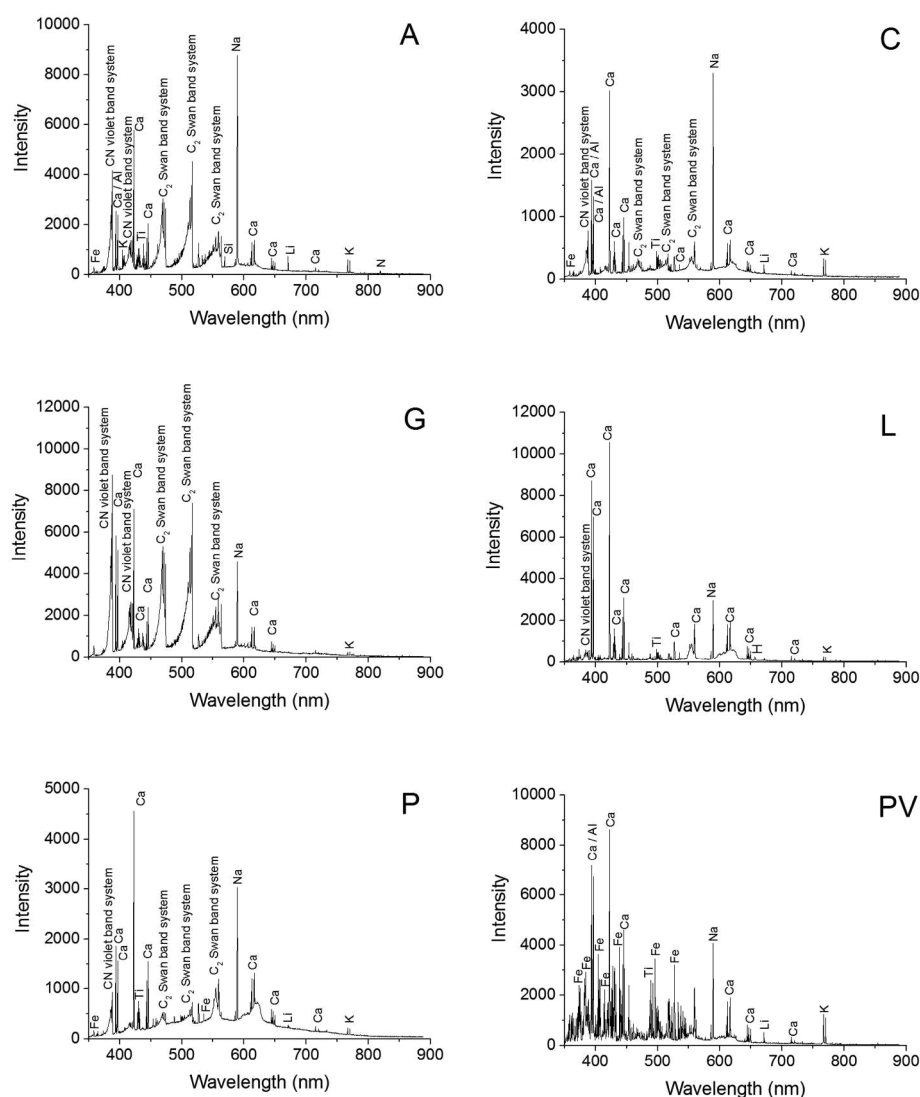
Figure 2. Single-pulse visible-range LIBS spectra of the studied coal samples (averaged spectra from 25 laser shots).

aluminum content. As expected, the most intense line in this spectral range is the C I 247.8 nm line. The intensity of this carbon line is highest in graphite and is one of the lowest in lignite; this is in correlation with the fixed carbon content of the samples (Table 1). The spectrum of sample PV deviates from the above in that it produces a line-rich spectrum with a low-intensity carbon line. The S/N ratio is generally good. The spectral background is elevated and has the appearance of two broad peaks centered at around ca. 250 and 300 nm.

The vis-range LIBS spectra were found to contain more spectral lines which were also significantly more intense (Figure 2). Intense carbon molecular bands, such as C_2 Swan bands and CN bands, also appear. These bands are most intense in graphite and anthracite. Interestingly, these molecular bands are almost completely absent in the spectrum of PV. Spectral lines of alkali and alkali-earth elements such as Ca, Na, K, Li, and Mg are also observable in all samples, and Ti and Al lines are also common. Fe lines are only detectable in great number in the sample PV. This clearly indicates a relatively high iron content of this coal sample, which is due to the fact that the Pécs-Vasas area (Hungary) in which this coal is mined is known to give iron ores as well.[28]

The above observations are in line with the sample properties listed in Table 1. For example, the PV brown coal has the highest ash content and one of the lowest carbon contents, which suggests a high mineral content. It may also be postulated that the CN and C_2 bands only appear with significant intensity in the spectra if the fixed carbon content is above 20−30%. Spectra from the Czech and Polish brown coal samples gave the lowest intensity spectra, which may be related to the high volatile matter content of these samples. The spectral background was largely silent except for the Polish brown coal. Based on the more characteristic nature of the vis-range spectra collected, we decided to include only the vis-range data in the statistical data evaluation described in later sections.

3.3. Correlation of Coal Composition and Spectral Features. One of the tentative uses of LIBS spectroscopy in applications which use coal fuel (e.g., heating and power generation) can be the direct prediction of the combustion-related properties of the fuel. The qualitative correlation of spectral features described in the preceding section, as well as similar successful literature attempts (e.g., refs 17 and 18), suggest that the approach may be successful.

The calorific value is the most important coal quality indicator. This indicator is a cumulative one, meaning that the heat

generated upon the combustion of a given amount (e.g., 1 kg) of coal comes from the oxidation of all combustible compounds present. In terms of coal proximate analysis nomenclature, the fixed carbon content characterizes the elemental carbon content of the sample, whereas the volatile matter content includes short-chain hydrocarbons, carbon monoxide and dioxide, hydrogen, sulfur, etc.[7] In general, most of the volatile matter content is combustible; thus, it also contributes to the calorific value. Thus, the total carbon content detected by LIBS spectroscopy (e.g., at carbon spectral lines) may be expected to reasonably correlate with the sum of the volatile matter and fixed carbon content and hence with the calorific value. The situation is complicated by the fact that the moisture content of samples is known to strongly suppress signal intensities in LIBS spectroscopy.[29,30] Consequently, low-rank coals (brown coals or lignites) with high moisture content may show too low spectral intensities. In addition to the C I 247.8 nm net line intensity, C_2 and CN band head net intensities may also be attempted to be used to predict the calorific value of coal samples. This use of the molecular bands is based on two factors: (a) that the nitrogen content in coal is well below 1% and (b) that laser ablation molecular isotope spectrometry (LAMIS) studies revealed that CN band head intensities are proportional to the carbon content of organic compound samples.[31] The CN band intensity was also successfully used for the analysis of UC in fly ash by LIBS.[16]

The set of graphs in Figure 3 show the experimental data obtained in this study for the above outlined correlations. Please note that no data is plotted for PV, as neither the fixed carbon content data nor the CN band intensity was available for this sample. As it can be seen in Figure 3a, the linear correlation between the sum of the volatile matter and fixed carbon content versus the calorific value is indeed quite good, as expected. At the same time, the plots with the normalized net intensity of the C I 247.8 nm line and the CN band head at 388.1 nm show poor correlation with the calorific value (Figure 4b,c). It is only for high rank coals (e.g., those with a calorific value above 6000 kCal/kg) that a reasonable estimate may be given for the calorific value based on the LIBS measurement of the CN band head intensity.

These findings suggest that more sophisticated multivariate modeling (such as PLS) is needed for the quantitative evaluation of the LIBS spectra for the purpose of the determination of combustion parameters. This was not pursued in the present study, but examples for this approach can be found in recent LIBS literature.[17,21]

3.4. Exploration of the Potential of LIBS for Indicating Coal Quality.

More than one potential way can be suggested as to how the statistical evaluation of LIBS spectroscopy data of coal fuel obtained in real-time on the site (e.g., at conveyor belts or feeding chutes, in depots, etc.) may be used to produce industrial control signals. These approaches are based on the information-rich (fingerprint-like) character of LIBS spectra, which can allow the assignment of coal type.

One of the suggested applications is the detection of a deviation from the expected coal quality. In this scenario, the statistical evaluation should be able to indicate that the LIBS spectrum of a coal sample (e.g., the coal being fed to the boiler) is significantly different from the stored spectrum of a reference coal (e.g., taken from the first batch of the fuel). In this application, only such statistical methods can be employed for the evaluation which can process the whole spectrum (e.g., a 2048-element data array). This is in fact not within the capacity of all methods; many multivariate methods can only process a
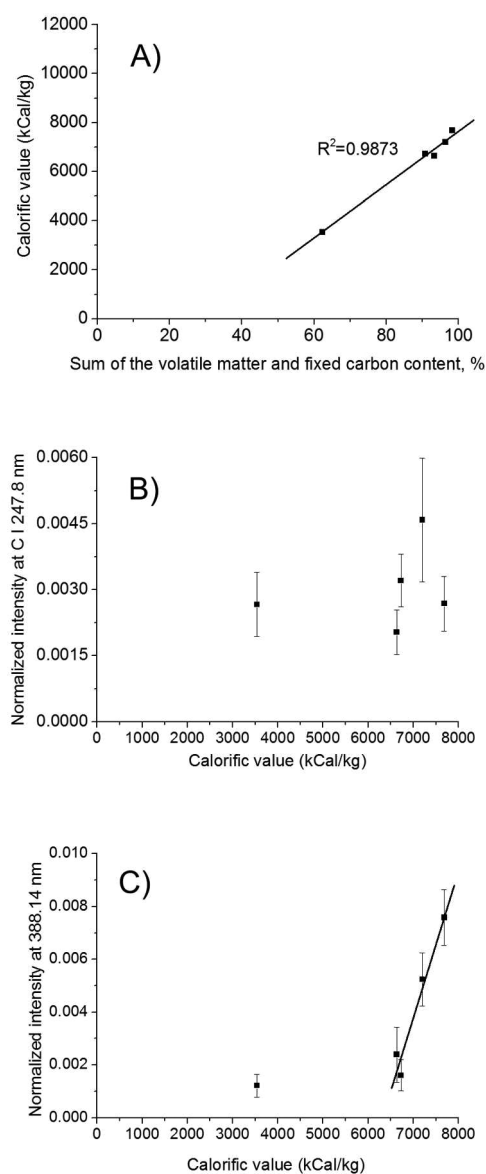
Figure 3. Correlations between the properties and LIBS spectral features of coal samples. a) The sum of the fixed carbon content and volatile matter content versus the calorific value, b) Net normalized intensity of the C I 247.8 nm spectral line versus the calorific value, c) Net normalized intensity of the CN band head at 388.1 nm versus the calorific value.
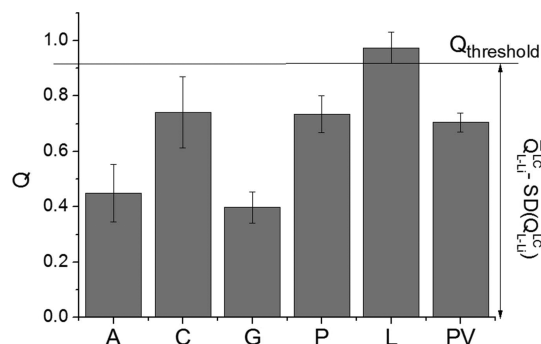
Figure 4. Graphical representation of the concept of testing the deviation from the expected coal quality (here lignite). Please see the text for further explanation.
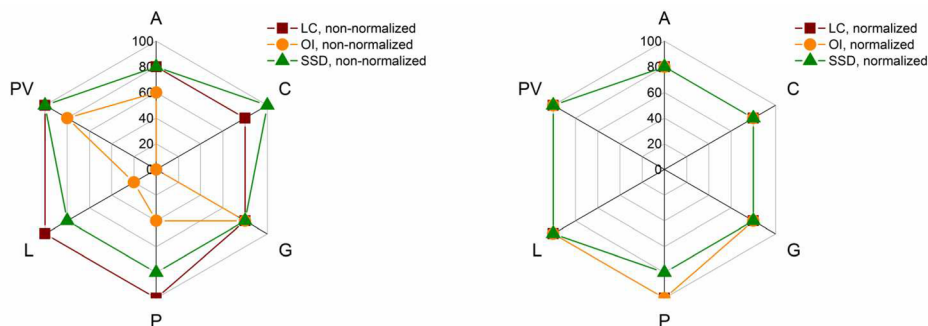
Figure 5. Results of the calculations in the detection of a deviation from the expected coal quality application by using the LC, OI, and SSD comparative functions. The graphs show on a percentage scale how many coal types could be differentiated from the reference coal type (the reference is indicated on the axes). The graph on the left refers to the case when raw spectra were evaluated, whereas the graph on the right refers to the case when spectrum normalization was employed prior to the evaluation. Please see the text for further explanation.

limited number of variables (e.g., less than the number of observations to be processed). Another useful application can be when the type of an unknown coal needs to be identified according to predefined classes (e.g., lignite, anthracite, etc.). Such a classification may require the use of a multivariate statistical method, which needs preprocessing (essentially some data reduction in the form of filtering, masking, etc.) of the spectral data sets. In the following subsections, we demonstrate how these two applications can be realized by employing various statistical approaches, and we characterize the performance of these methods.

3.4.1. Detection of a Deviation from the Expected Coal Quality. We tested the linear correlation (LC), sum of squared deviation (SSD), and overlapping integral (OI) comparative methods in this application. All three corresponding functions (degree of similarity, Q, as defined in section 2.3) are easy to compute and can be applied to the complete spectra.

In order to reliably assess the performance of the comparative functions in this application, we carried out the comparison of all six coal qualities in every possible combinations on the 25 spectra recorded for each type. This meant that the Q values with all of the LC, SSD, and OI methods were calculated when one of the coal qualities was taken as reference (defined as the average of the spectra recorded for that coal type) and was compared to each individual spectra within all six types. For example, when lignite, sample L, was the reference and LC was the comparative function then all six comparisons, namely, $Q^{LC}_{L-L,i} = \bar{L} \overset{LC}{\leftrightarrow} L_i$, $Q^{LC}_{L-A,i} = \bar{L} \overset{LC}{\leftrightarrow} A_i$, $Q^{LC}_{L-P,i} = \bar{L} \overset{LC}{\leftrightarrow} P_i$, $Q^{LC}_{L-C,i} = \bar{L} \overset{LC}{\leftrightarrow} C_i$, $Q^{LC}_{L-PV,i} = \bar{L} \overset{LC}{\leftrightarrow} PV_i$, $Q^{LC}_{L-G,i} = \bar{L} \overset{LC}{\leftrightarrow} G_i$, were computed, where $\bar{L}$ is the average of the 25 lignite spectra and X_i are the individual spectra recorded for coal type X. Index i runs from 1 to 25. This resulted in 6×2 data arrays which included the average of the Q values obtained from the comparisons and their respective standard deviations. In the case of the above example, the elements of the data array were as follows:

$$\bar{Q}^{LC}_{L-L,i};\ SD(Q^{LC}_{L-L,i})$$

$$\bar{Q}^{LC}_{L-A,i};\ SD(Q^{LC}_{L-A,i})$$

$$\bar{Q}^{LC}_{L-P,i};\ SD(Q^{LC}_{L-P,i})$$

$$\bar{Q}^{LC}_{L-C,i};\ SD(Q^{LC}_{L-C,i})$$

$$\bar{Q}^{LC}_{L-PV,i};\ SD(Q^{LC}_{L-PV,i})$$

$$\bar{Q}^{LC}_{L-G,i};\ SD(Q^{LC}_{L-G,i})$$

where SD designates the standard deviation. The calculations were also repeated after spectrum normalization, which is often employed in LIBS spectroscopy to correct for fluctuations in e.g. pulse energies or focusing conditions.[12,13] Thus, a total of $6 \cdot 3 \cdot 2 = 36$ data arrays were produced (6 sample types, 3 comparative functions, and 2 statuses of spectrum normalization).

The evaluation was done by defining a $Q_{threshold}$ for each data array and counting the percentage of how many $\bar{Q} + SD(Q_i)$ values in the same array were lower than this. Logically, $Q_{threshold}$ was taken as the $\bar{Q} - SD(Q_i)$ value for the case when the reference coal type is compared to itself (this case gives the highest degree of similarity). In the above LC/lignite example, this means that $Q^{LC}_{L,threshold} = \bar{Q}^{LC}_{L-L,i} - SD(Q^{LC}_{L-L,i})$. A graphical representation of the concept can be seen in Figure 4. This evaluation gives an indication of the degree of separation of the reference from the rest of the sample types on a percentage scale running from 0 to 100%, where 100% means that all other coal types can be fully discriminated from the reference (but not necessarily from each other). This may also be called as "the accuracy of discrimination". The results of these calculations for all combinations as described above can be seen in Figure 5.

It can be seen in Figure 5 that the non-normalized spectra method OI gives the poorest performance, whereas methods LC and SSD perform well. The accuracy of the latter two is at least 80%, irrespective of the reference. In contrast, spectrum normalization greatly improved the accuracy of methods OI and SSD. The accuracy of method LC, which was already good, did not improve after normalization. In fact, the performance of the LC was identical with or without spectrum normalization, which was to be expected as the linear correlation function is known to be fully insensitive to the linear transformation of the compared data sets,[32] and spectrum normalization falls under this category.

In summary, it can be stated that the set goal of detecting a deviation from the expected coal quality (discrimination of a reference type from all other types) can be done with good (≥80%) accuracy by using the tested methods, but especially by the LC method and irrespective of the reference. Of course, these results can be easily transformed to the case when only two coal types are to be discriminated from each other (e.g., actual coal fuel and reference coal fuel).
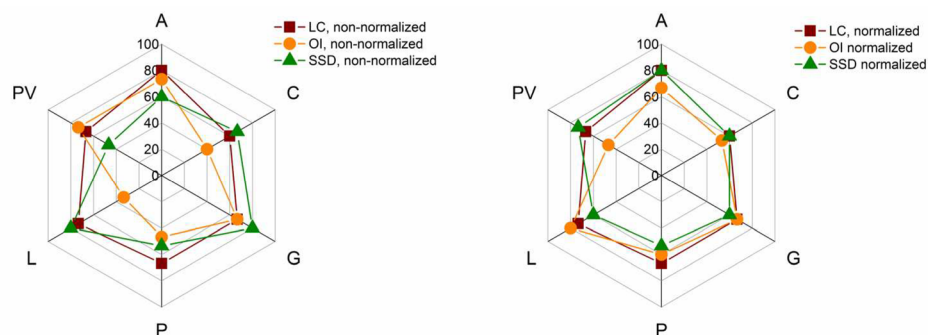
Figure 6. Results of the calculations in the discrimination of coal quality application by using the LC, OI, and SSD comparative functions. The graphs show on a percentage scale how successfully can all coal types be differentiated from each other based on their Q (degree of similarity) value when performing the comparisons using a certain reference coal type (indicated on the axes). A 100% accuracy of discrimination in these graphs would indicate that the ranges of Q ± SD are mutually exclusive for all coal types (complete discrimination). The graph on the left refers to the case when raw spectra were evaluated, whereas the graph on the right refers to the case when spectrum normalization was employed prior to the evaluation. Please see the text for further explanation.

3.4.2. Discrimination Based on the Use of Comparative Functions. We tested the performance of the comparative functions (LC, SSD, and OI) in this application too. The same 6 × 2 data arrays with Q values were used described above were used, the only difference was that the evaluation of the data array was done in a different way.

In this evaluation, the discrimination accuracy is better if the overlap between the $\overline{Q}_i \pm SD(Q_i)$ is smaller within the same data array; 100% accuracy is achieved if all $\overline{Q}_i \pm SD(Q_i)$ ranges are fully disjunct. This was computed by performing pairwise range comparisons within the array in all possible combinations (15) and counting the percentage of the number of disjunct ranges.

The results found are shown in Figure 6. As can be seen, the performance of the comparative functions were significantly poorer in this application. The accuracy of discrimination was 40−80% and was greatly influenced by the reference. These findings suggest unstability. Spectrum normalization did bring some improvement (except for the LC method), as it increased the accuracy to 50−80%. Nevertheless, the results indicate that the performance of these comparative functions is not enough for this challenging application.

3.4.3. Discrimination Based on the Use of Linear Discriminant Analysis. More powerful discrimination can be achieved by using multivariate statistical methods. In this study we tested the use of LDA, which was already found to be effective for the discrimination of various sample types in the LIBS literature, such as alloys,[33] bricks,[34] biominerals,[35] or soil.[36] Prior to LDA, a data reduction of the training data set is necessary, as the number of variables (2048, the length of the spectrum array) largely exceeds the number of observations (150, which is 6 samples with 25 spectra for each). For such data reduction, several potential methods, supervised or unsupervised, are suggested in the LIBS literature. These include binning (summing or averaging of spectral bands to decrease spectral resolution), stepwise optimization (by sequentially omitting a random part of the data set until the best accuracy of LDA performance is achieved),[37] the combination of the evaluation with principal component analysis,[34,35] or the manual selection of relevant spectral features. We adopted the latter method in the present study and selected 18 spectral features (wavelengths) associated with major and minor components present in coal samples. The selection was based on the visual comparison of the 6 coal spectra (each an average from 25 individual spectra taken

of the same sample) and on searching for features which are present with reasonable but different intensities in most spectra. Atomic and ionic lines as well as molecular bands were also included in the selection. As was alluded to before, we only used the vis-range spectra for the statistical evaluation. Table 2 lists the variables selected and retained in the spectra.

Table 2. Selected Wavelengths (Variables) in LIBS Spectra of Coal Samples for the Purposes of Multivariate Statistical Evaluation

wavelength (nm)	assignment	wavelength (nm)	assignment
388.1	CN	484.0	Fe, Ti
403.2	Fe, Ti	487.8	Fe, Ti, Ca
422.6	Ca	568.8	Si, Na
424.9	Ti	670.8	Li
426.0	Ti	766.6	K
455.1	Ti	769.8	K
460.8	Fe	818.2	N
469.6	C_2	819.4	Na
475.7	Ti	854.2	Ca

The cumulative percentage of variance for the first three canonical discriminant functions was found to be 89.54%, and with the addition of the fourth and fifth one, it increased to 100%. The Wilk's lambda test gave a dimensionality of 5 at the 0.05 level; therefore, all LDA results here were calculated using 5 canonical variables (canonical discriminant functions). The fact that the first three variables account for nearly 90% of the variance justifies the graphical illustration of the classification results in a three-dimensional coordinate system, which is the largest dimensionality that can be visually interpreted (Figure 7). The error rate for the classification of training data was excellent: 2.67%. As it can also be seen in Figure 7, out of the 150 observations, there is a very slight (one-member) overlap between classes C and P and between P and L.

A cross-validation test of the discrimination results was also performed, which gave the results in Table 3. The overall error rate was found to be as low as 4.67%; thus, the model correctly classified the samples in 95.33% of the cases. The accuracy was 92% or better in all groups (Table 3.).
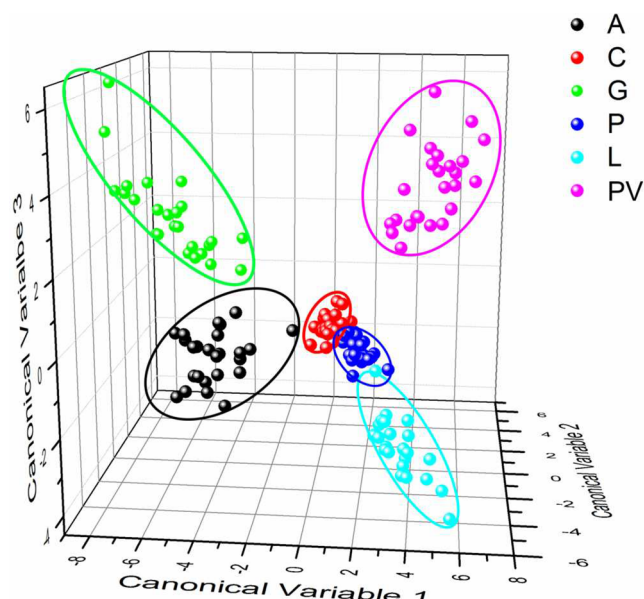
Figure 7. 3D representation of the classification results from LDA, plotting the first three canonical discriminant functions (canonical variables), which cumulatively account for 89.54% of the variances. Please note that the calculations were done by using 5 variables. The ellipses drawn are only meant to guide the eye.

Table 3. LDA Cross-Validation Results for the Coal Samples[a]

		Predicted group					
		A	C	G	P	L	PV	Total
A		23	1	1	0	0	0	25
		92.00%	4.00%	4.00%	0.00%	0.00%	0.00%	100.00%
C		0	24	0	1	0	0	25
		0.00%	96.00%	0.00%	4.00%	0.00%	0.00%	100.00%
G		0	0	24	1	0	0	25
		0.00%	0.00%	96.00%	4.00%	0.00%	0.00%	100.00%
P		0	1	0	24	0	0	25
		0.00%	4.00%	0.00%	96.00%	0.00%	0.00%	100.00%
L		0	1	0	0	23	1	25
		0.00%	4.00%	0.00%	0.00%	92.00%	4.00%	100.00%
PV		0	0	0	0	0	25	25
		0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	100.00%
Total		23	27	25	26	23	26	150
		15.33%	18.00%	16.67%	17.33%	15.33%	17.33%	100.00%

[a]The right-justified integers in the columns indicate the number of samples assigned to that group, whereas the percentages show the rate of correct assignations. The number of correct assignations for each group are highlighted in orange. Each group contained 25 observations; thus, the total number of observations was 150.

4. CONCLUSIONS

In this study we assessed the capabilities of LIBS in the application of the qualitative analysis of coals, in view of the potential use of LIBS for the quality control of coals in coal-fired power plants or coal preparation (and handling) plants. The experiments were carried out in the laboratory, using six different coal samples obtained from commercial sources in Hungary and a compact LIBS system. First, the spectral features and their repeatability were studied, and the qualitative discrimination analysis of the coals was then investigated by using three different comparative statistical functions (via the direct comparison of the

similarity/dissimilarity of spectra) and also by canonical linear discriminant analysis.

It was found that the comparative functions are successfully applicable (with at least 80% accuracy) to decide whether the compared two coals were of the same type or not. This can be exploited, for instance, by implementing a simple LIBS-based monitoring technique in a power or handling plant to identify a deviation from the expected (reference) fuel quality, similar to the control chart methodology. The comparative functions are easy to calculate, and the discrimination result is based on the whole (visible-range) LIBS spectrum; thus, no complicated or operator-driven data reduction is necessary. Consequently, the technique is fast, robust, and flexible. However, in the more challenging application of the direct classification of coal types, the comparative functions showed insufficient and unstable performance.

At the same time, canonical linear discriminant analysis was found to be highly efficient. Using five canonical variables and after reducing the spectra to 18 variables (to retain the spectral intensity of selected atomic lines of common elements in coal, CN and C_2 band heads), the achieved classification accuracy was 95.33% according to the cross-validation test of the model. This multivariate approach provides a clearly superior accuracy; however, it is at the cost of the necessity of a "supervised" data reduction. Nevertheless, the computing and database demands of this approach can also be easily fulfilled; thus, the automation of this approach can also be implemented. The described results clearly indicate that LIBS spectroscopy can be used for the quality control of coals and that thereby LIBS data can also indirectly contribute to the control of the combustion process.

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Notes

The authors declare no competing financial interest.

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