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Laser-Induced Breakdown Spectroscopy Assisted Chemometric Methods for Iron Ores Classification and Identification

LI-YI CHEN, CHUN-HSUN LIN and TIAN-YUAN LIANG

New Materials Research & Development Department,
China Steel Corporation

Quality control of iron ore grades is an important part of the iron making process. Fast and accurate analysis techniques must be established to identify and classify the chemical property and composition of iron ore grade in the integrated steel plant. The aim of this work is to develop laser-induced breakdown spectroscopy (LIBS) assisted chemometric methods for fast classification and identification of iron ores. Five types of iron ore standards were selected and their LIBS spectra were recorded for chemometrics investigation. In addition, nine feature lines were extracted from the LIBS spectra of iron ore by using principal component analysis (PCA). Partial least squares discriminant analysis (PLS-DA) was then introduced to establish a discrimination model for classifying the five types of iron ores based on the nine feature lines, and showed the correct discrimination rates of 83.3%. Finally, the model was applied to discriminate three types of iron ores from stockpiles in China Steel Corporation (CSC) and showed the great potential for identification and classification. The research revealed that LIBS technology assisted with chemometrics will provide a fast method for quality control of iron ore.

Keywords: Iron ore, LIBS, Chemometrics, PCA, PLS-DA

1. INTRODUCTION

Laser-induced breakdown spectroscopy (LIBS) is a promising atomic emission spectroscopic technique[1], especially in green chemistry analysis. Briefly, a focused laser pulse strikes the sample surface and creates a ball of microplasma. Then, the plasma cooled and emitted unique spectral light peaks that can be used as spectral features to identify the element in the sample. It has many advantages for sample analysis, including (1) adaptable for all types of samples, such as solids, liquids, and gases, (2) reduced sample preparation procedure, (3) simultaneous multi-element analysis, (4) in situ remote analysis. It also has broad applicability for many fields, such as mineral selection[2-4], aerospace exploration[1], industrial analysis[5-7], and environmental monitoring[3,8-10].

Iron ore is an important raw material in the metallurgical industry. Iron ore grades mostly depends on the content of iron and minor impurities, such as silica, alumina, and phosphorus. In addition, high grade iron ores helps to maximize the blast furnace yield and even decrease the defects in end-products[11]. Therefore, the identification and classification of iron ore is the most important step in quality control. In general, the element content of iron ore should be identified in both qualitative and quantitative methods[12]. However, it is time-consuming and requires complicated sample preparation. In order to rapidly classify the iron ore grades, the LIBS technique can be adapted to provide feedback of quality information of the process in real time.

Due to LIBS being a powerful spectroscopic technique, it provides several thousands to tens of thousands of element-related variables per spectrum. Recently, LIBS spectroscopy coupled with chemometrics has shown great potential in reducing high dimensional data to a lower dimensional factor[13]. There are several chemometric approaches that had been applied to LIBS spectral analysis and classification. For example, partial least squares discriminant analysis (PLS-DA) has been used for classifying rocks[14], soils[14], coffee[15], and explosives[16] based on LIBS spectra. In addition, soft independent modeling of class analogy (SIMCA) has also been used to differentiate between bacterial spores[17], molds[17], and nerve agent simulants[18]. In addition, PLS-DA has been shown to offer the best classification results compared to PCA and SIMCA, because PLS-DA can maximize the inter-class variance while minimize the intra-class variance[19].

In this study, we developed a discrimination model based on LIBS technique coupled with a chemometric method for identification and classification of iron ores. The chemometric methods of PCA and PLS-DA were both introduced to conduct the LIBS feature extraction and discrimination analysis. Therefore, the selected

feature spectral lines were verified.

2. EXPERIMENTAL METHOD

2.1 Experimental device and LIBS data acquisition

The measurements were performed by using a J200 LIBS instrument (Applied Spectra, USA) equipped with a pulsed Nd:YAG laser, an optical microscope, a 6-channel CCD spectrometer, an adjustable X-Y-Z moving stage, and a personal computer with a laser operating system software and Clarity LIBS software for quantitative analysis.

All of the experiments were carried out in an air environment. The focused sample area was irradiated by pulsed laser with a repetition frequency of 10 Hz, energy of 12 mJ, and wavelength of 266 nm. After the irradiation, the light emitted from the sample micro-plasma was collected and the spectrum at wavelengths of 200-850 nm was recorded by a 6-channel spectrometer coupled with CCD camera. The delay generator provided a proper delay time to eliminate the initial continuum emission. For all measurements, the gate width and exposure time of the CCD were set to 1.050 ms and 1 μs, respectively.

Each spectrum was collected by an accumulation of 23 laser pulses per site to increase the signal-to-noise ratio (SNR). Each sample was analyzed by 60 different sites (60 spectra were obtained). Furthermore, 60 LIBS spectra were recorded from each type. Thus, a total of 300 LIBS spectra were gathered from five types of iron ore standards.

2.2 Iron ore samples

Five types of iron ore standards were used in this study: SRM 692 (NIST, USA), JSS-800-3 (ISIJ, Japan), BAM 678-1(BAM, Germany), CECA 677-1 (EURONORM-CRM, EU), and ECRM 681-1(BAS, UK). Three types of iron ores from China Steel Corporation (CSC): RH.F, Caraja.F, and HY.F. The certified elemental compositions of the main oxide materials in standard samples are presented in Table 1.

To obtain the homogenous and compact surface of the iron ore for laser ablation, 3g iron ore powder was blended with 5% PVB solution and then made into the cylindrical pellets (Ø= 32mm) through automatic hydraulic press (Atlas Autotouch, Specac, UK) with sufficient pressure (12T) lasting 30 seconds.

2.3 Chemometric Methods

Principal component analysis (PCA) is an unsupervised multivariate method that extracts useful information and describes major trends by finding new combinations of variables of the data set. When the intensity of a series of emission lines is used as an input variable, the new variable generated by PCA analysis can be named as principal components and ranked according to the explained variances. For example, the first principal component (PC1) explained most of the variances, and followed by the second PC, the third PC, and so on. Besides, the score and loading plot based on different components are also used to indicate the group distribution of sample set and the variable effect on each component, respectively.

Partial least squares-discriminant analysis (PLS-DA) is a discrimination method based on partial least squares regression (PLSR). PLSR is applied to explore the linear relationship between the variables of the spectral data and the corresponding features, such as chemical content. The new orthogonal variables called latent variables (LVs) are selected to maximize the covariance. When PLS-DA is conducting the regression procedure, the prediction value of PLS-DA was a real number. Thus, a threshold value should be set to determine which category it belongs to. In this study, the threshold value was set to 0.5.

3. RESULTS AND DISCUSSION

3.1 Overview of iron ore LIBS spectra

In this study, five iron ore standards of SRM 692, JSS-800-3, BAM 678-1, CECA 677-1, and ECRM 681-

Table 1 Certified element composition of five iron ore standards (wt%).

Sample name	Composition wt%								
	T.Fe	SiO_2	CaO	MgO	Al_2O_3	TiO_2	Na_2O	K_2O	MnO
SRM 692	59.58	10.14	0.02	0.04	1.41	0.05	0.01	0.04	0.46
JSS-800-3	62.85	2.60	0.02	0.22	2.01	0.08	--	--	0.28
ECRM 681-1	33.21	17.80	3.92	1.48	10.62	0.48	0.09	0.59	0.28
BAM 678-1	60.75	3.70	5.48	0.95	0.53	0.22	0.15	0.13	0.10
CECA 677-1	51.54	25.19	0.05	0.02	0.60	0.02	0.01	0.01	0.02

1 were selected as five different classes. The LIBS spectra of these standards were recorded for setting the parameter of classification. As shown in Figure 1, the five LIBS spectra in the range of 200−850 nm had similar profiles except for the spectral intensity. The main spectral lines were located around the region of 240−440 nm and 480−560 nm. There were obvious peaks around 590 nm and 770 nm.

Because the iron ores possess the homologous matrix of chemical and elemental composition, they exhibited the similar LIBS spectra curves. In order to analyze information of the LIBS spectral lines, NIST Atomic spectra database were utilized to identify and label the majority of the emission lines of the spectra. A typical spectrum of JSS-800-3 was shown in Figure 2, which revealed the characteristics of emission spectral lines of Fe located in a broad range of 360-440 nm wavelength. A number of emission lines with different LIBS intensity were also observed to contain the information of Al, Ca, Si, Na, Ti, K elements.

3.2 Principal components analysis on LIBS data

In order to classify the iron ore standards, it is necessary to extract the LIBS spectral features of these five standards for multivariate analysis. First, PCA analysis was employed to transform the full spectra into several principal components (PCs). From the loading plot of the PCA analysis, most of the emission lines of the main elements in each spectrum have large load coefficients. Then, we selected nine emission lines with high signal-to-noise ratio from the LIBS spectra, which were labeled as Si I 288.16 nm, Ti II 328.77 nm, Ca II 393.37 nm, Al I 394.40 nm, Mn I 423.51 nm, Fe I 438.35 nm, Mg I 518.36 nm, Na I 588.99 nm, and K I 766.49 nm (I: atomic spectral lines and II: ionic spectral lines). Therefore, the labeled emission lines represented the LIBS feature lines of Si, Al, Fe, Mg, Na, Ca, K, Ti, and Mn of each iron ore standard class. Thus, a matrix with 300×9 (LIBS spectra×lines) was obtained for further analysis. Another PCA analysis was executed with the nine feature lines of each LIBS spectral data to display any variation among the five standards. The score plot of the first two PCs shown in Figure 3(a) exhibited an apparent clustering of each iron ore class. The first two PCs explained 87% (PC1:58.5 %, PC2:28.5 %) of the variations among total spectral information. In addition, the loading plot of PCA also revealed the importance of the analyzed variables. As shown in Figure 3(b), there were
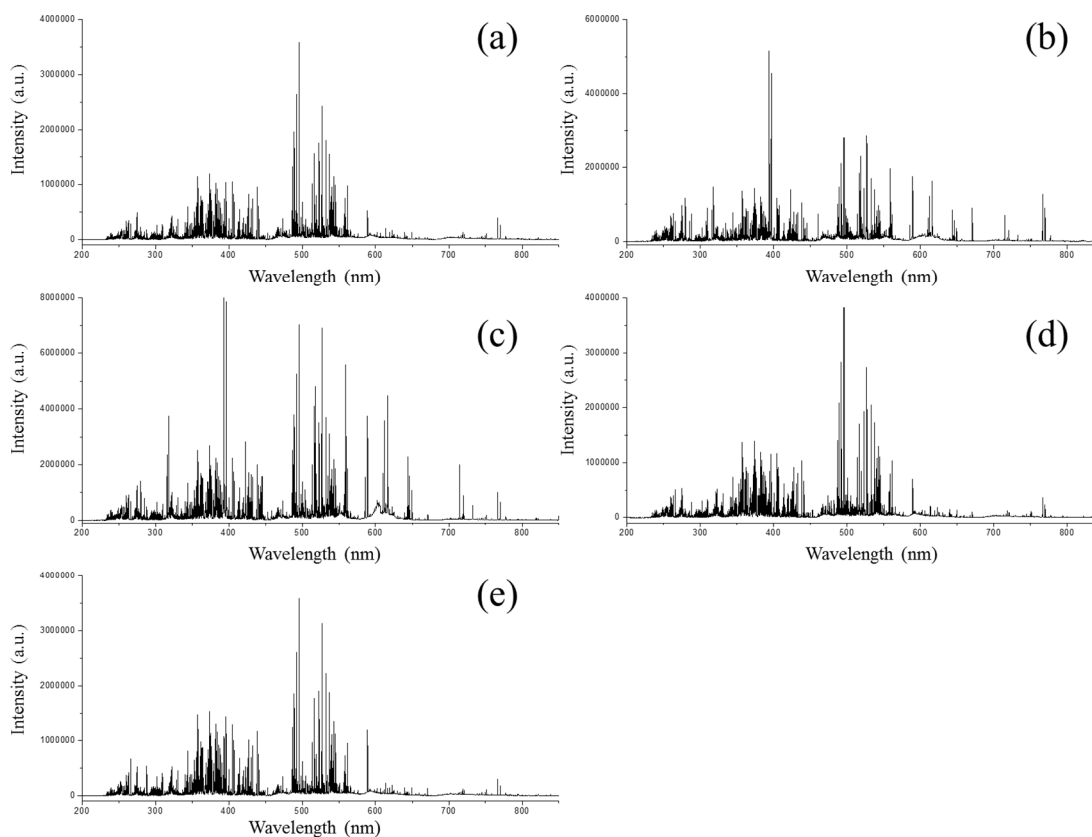

Fig.1. Representative LIBS spectra of the iron ore standards, (a) JSS-800-3, (b) ECRM 681-1, (c) BAM 678-1, (d) SRM 692, (e) CECA 677-1.
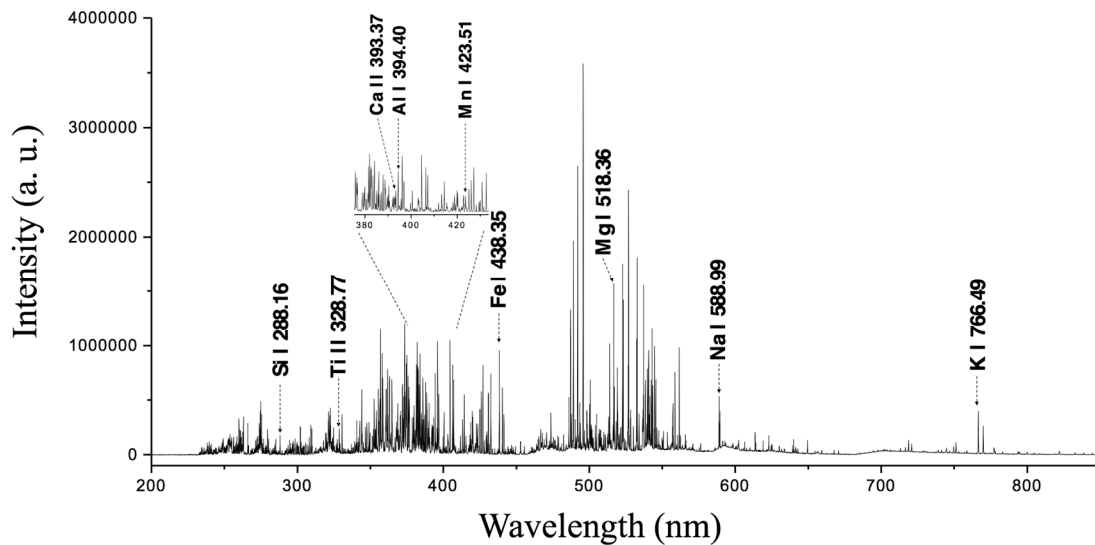
Fig.2.   The main emission lines in LIBS spectrum of JSS-800-3. (I: atomic spectral lines and II: ionic spectral lines)
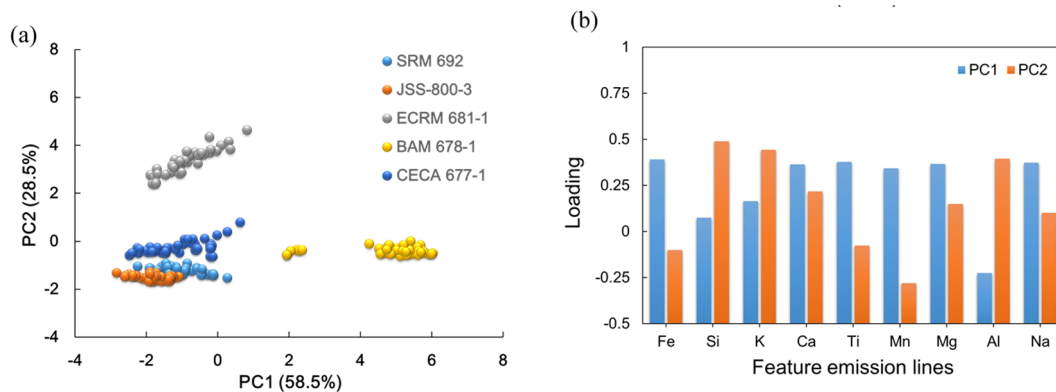

Fig.3.   The score plot (a) and loading diagram (b) of first two PCs from PCA on LIBS spectra with the selected emission lines of five iron ore standards.

six variables of Ca, Mg, Na, Ti, Fe, and Mn, which showed the similar contribution on PC1. The variables of Al, Si, K showed the dominating contribution on PC2. For fully explaining the score plot, Table 1 was conducted to analyze the scatter distribution of the five classes of iron ores. The BAM 678-1 class with relatively high concentration of Fe, Ca, Na and low concentration of Al was located in the positive side of PC1 and the negative side of PC2. On the contrary, the ECRM 681-1 class with a low concentration of Fe and relatively high concentration of Al, Si, K was located in the negative side of PC1 and the positive side of PC2. In addition, the three classes of SRM 692, JSS-800-3 and CECA 677-1 with relatively low concentration of Ca compared with ECRM 681-1 and BAM 678-1 class were both located in the negative side of PC1 and PC2.

3.3 PLS-DA Classification Model

Despite the PCA analysis being able to identify the differences of iron ores, PLS-DA based chemometric method was further employed to discriminate the classes of iron ore. Prior to build PLS-DA classification model with the variables from the 9 feature lines, the labeled classes corresponding to each spectrum were divided into calibration sets and prediction sets which contained 30 LIBS spectra, respectively. As shown in Table 2, the prediction accuracy of the PLS-DA model was 83.3% of SRM 692, JSS-800-3, BAM 678-1, CECA 677-1, and ECRM 681-1, with 7 LVs. The results indicated the feasibility of identifying the varieties of iron ore by using the feature lines that correspond to the elements. Furthermore, in order to verify the accuracy and reliability of the PLS-DA classification model, we collected 3 types of iron ores from CSC stockpiles, RH.F, Caraja. F, and HY.F, and performed the discriminant analysis. The results are shown in Table 3 and the prediction accuracy

Table 2   The prediction accuracy of five iron ore standards calculated by PLS-DA.

Sample name	Prediction Accuracy		
	No. of Samples	No. of Misclassified Classification	Rate of Correct Classification (%)
SRM 692	30	22	73.3
JSS-800-3	30	30	100
ECRM 681-1	30	29	96.7
BAM 678-1	30	29	96.7
CECA 677-1	30	15	51.7
Total	150	125	83.3

Table 3   The prediction accuracy of CSC iron ore samples calculated by PLS-DA.

Sample name	Prediction Accuracy		
	No. of Samples	No. of Misclassified Classification	Rate of Correct Classification (%)
RH.F	30	0	100
Caraja.F	30	0	100
HY.F	30	0	100
Total	90	0	100

was 100% of all the CSC iron samples. Thus, it could be concluded that there was an obvious differentiation in 3 types of CSC iron ores and the selected 9 feature lines were valid to distinguish the different iron ores.

4. CONCLUSIONS

Quality control of iron ore grades is an important part of the iron making process in the metallurgical industry. This study establishes a LIBS based chemometrics method for the identification and classification of iron ore samples. PCA and PLS-DA are both conducted to process the related variables of LIBS spectra for classification and prediction of five iron ore standards. In order to simplify the discrimination model, the full spectra of the iron ore standards are analyzed by PCA and 9 feature lines are extracted (Si I 288.16 nm, Ti II 328.77 nm, Ca II 393.37 nm, Al I 394.40 nm, Mn I 423.51 nm, Fe I 438.35 nm, Mg I 518.36 nm, Na I 588.99 nm, and K I 766.49 nm) for further analysis. Then, a PLS-DA discrimination model of iron ores is well established with the 9 feature lines as the input variable for classification. Moreover, the PLS-DA model is further used to identify the other 3 iron ore samples from CSC stockpiles, which verified the feasibility of applying the model to classify the iron ore in the metallurgical industry.

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