JAAS

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/jaas

ARTICLE TYPE

Quantitative and classification analysis of slag samples by Laser-induced breakdown spectroscopy(LIBS) coupled with support vector machine(SVM) and partial least square(PLS) methods

Tianlong Zhang[a], Shan Wu[a], Juan Dong[a], Jiao Wei[a], Kang Wang[b], Hongsheng Tang[a], Xiaofeng Yang[c], Hua Li*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Laser induced breakdown spectroscopy(LIBS) technique coupled with support vector machine(SVM) and partial least square(PLS) methods was proposed to perform quantitative and classification analysis of 20 slag samples. The characteristic line (Ca, Si, Al, Mg and Ti) of LIBS spectra for slag samples can be identified based on NIST database. At first, quantitative analysis of the major components(Fe_2O_3, CaO, SiO_2, Al_2O_3, MgO and TiO_2) in slag samples was completed by SVM with the full spectra as input variable, and two parameters(kernel parameter of RBF-**γ** and $\boldsymbol{\sigma^2}$) of SVM were optimized by grid search(GS) approach based on 5-fold cross-validation(CV). The performance of SVM calibration model was investigated by 5-fold CV, the prediction accuracy and root mean square error(RMSE) of SVM and PLS were employed to validate the predictive ability of multivariate SVM calibration model in slag. SVM model can eliminate the influence of nonlinear factors due to self-absorption in the plasma and provide a better predictive result. And then, two type of slag samples(open-hearth furnace slag and high titanium slag) were identified and classified by partial least squares-discrimination analysis(PLS-DA) method with different input variables, sensitivity, specificity and accuracy were calculated to evaluate the classification performance of PLS-DA model for slag samples. It has been confirms that LIBS technique coupled with SVM and PLS methods is promising approach to achieve the online analysis and process control of slag and even metallurgy field.

1. Introduction

Slag is an significant product in the steel-making industry, and determines the quantity and performance of steel product. In the process of metal smelting, the real-time monitoring of slag is of great significant to ensure performance of molten steel, determine whether it is reached to the end of smelting, and reduce energy consumption. The major component of slag include CaO, SiO_2, Al_2O_3, MgO, Fe_2O_3, TiO_2 and so on. Conventional approaches of slag analysis mainly include:[1-6] chemical analysis, X-ray fluorescence(XRF), inductively coupled plasma optical emission spectroscopy(ICP-OES), mass spectroscopy(MS) and so on. However, these approaches require complicated sample preparation and much analysis time, which fails to timely obtain the information of steel product, and even hinders their application for real time and fast analysis.

Laser induced breakdown spectroscopy(LIBS) is one of the most valuable and prospect analysis technique based on laser plasma spectral with capable of quantitative and classification detection. Compared with conventional analytical techniques, the LIBS technique bears some obvious advantages,[7-9] such as multi-elemental simultaneous analysis, all types of the samples (solids, liquids, and gases) can be analyzed, less sample requirement and minimal sample preparation. At present, the LIBS technology has become an international research focus in the metallurgical analysis.[10-12] The application of LIBS technique to metallurgical industry includes iron ore selection,[14,15] process control,[16,17] iron slag analysis[18-21] and so on.

The slag analysis on LIBS refers to classification and quantitative analysis. The classification of slag samples can be fulfilled depends on difference of its major component and corresponding concentration. In other words, it is completed by the difference comes from spectra integrated intensity and wavelength of LIBS spectra. However, quantitative analysis of slags is employed to detect the concentration of certain component or element of unknown slag samples. The quantitative analysis methods of slag on LIBS include internal standard method, calibration-free(CF)[20,22] and multivariate calibration methods,[19] which is completed by constructing the relationship between the integrated intensity of the analysis line or intensity ratio(analysis line vs reference line) of interest element and the known concentration of a set of calibration samples, whereas CF assumes local thermodynamic equilibrium(LTE) in the laser plasma to calculate its plasma temperature, from which the composition of the sample is then derived, regardless of the matrix effect. The internal standard method and CF are univariate and established by using the intensity of single feature lines and the corresponding concentration of the certain component or element. However, the univariate calibration model often fails to meet requirement of the quantitative analysis due to the fluctuation of laser energy, the inhomogeneity of samples and complex matrix effect.[22] The chemical composition of slag sample is always affected by many matrix effects. There are serious overlapping spectral peak of the spectrum in the iron substrate, and the traditional univariate calibration model can't eliminate the impact of these interference factors. Multivariate calibration method is an effective tool to overcome matrix effect for complex sample. At present, multivariate calibration methods for slag analysis was partial least squares(PLS).[19] However, support vector machines(SVM) is a new and promising classification and regression method proposed by Vapnik.[23] It was originally developed for classification problems, but can also be extended to solve non-linear regression problems by means of ε-insensitive loss function.

The present work explores the combination of LIBS technology coupled with SVM and PLS method for quantitative and classification analysis of slag samples. A series of 20 slag samples were compressed into pellets and prepared for LIBS measurement. At first, quantitative analysis of the major components(Fe_2O_3, CaO, SiO_2, Al_2O_3, MgO, MnO_2 and TiO_2) in slag samples was completed by SVM with the full spectra as input variable, and two parameters of SVM model were optimized by grid search(GS) approach. The performance of SVM calibration model was investigated by 5-fold CV, the prediction accuracy and root mean square error(RMSE) of SVM and PLS were employed to validate the predictive ability of SVM calibration model in slag. And then, two type of slag samples(open-hearth furnace slag and high titanium slag) were identified and classified by PLS-DA method with different input variables, sensitivity, specificity and accuracy were calculated to evaluate the classification performance of PLS-DA model for slag samples.

2. Methodology

2.1. LIBS setup and acquisition conditions

The detailed description of LIBS setup was shown in the previous works.[24] A Q-switched Nd: YAG laser(λ=1064nm, 10 ns pulse FWHM, 80 mJ/pulse, repetition rate of 5 Hz) was used to generate the plasma in air at atmosphere pressure on the pellets. The pellet was placed directly on an X-Y-Z manual micrometric stage. The pulse laser beam was focused onto the slag sample surface vertically by a 50mm focal-distance lens, which was generated a spot of about 0.2 mm diameter. The emission from the plasma created was collected with a 4-mm aperture, with a 7mm focus fused silica collimator placed at 45° angel with respect to the laser pulses and a distance of 3 cm from the sample, and then focused into an optical fiber, which was coupled to the entrance of the Echelle spectrometer Aryelle 400 (LTB, German). The spectrometer provides a constant spectral resolution (CSR) of 6000 over a wavelength range 220-800nm displayable in a single spectrum. An electron-multiplying CCD(EMCCD) camera (QImaging, UV enhanced, 1004 ×1002 Pixels, USA) coupled to the spectrometer was used for detection of the dispersed light. Intensity and wavelength were calibrated by Hg-Ar lamps equipped with LTB 400 spectrometer. The overall linear dispersion of the spectrometer camera system ranges from 37 pm/pixel(at 220nm) to 133pm/pixel(at 800nm). To prevent the EMCCD from detecting the early plasma continuum, a mechanical chopper is used in front of the entrance slit. The experiments were carried out under atmosphere condition, and the gate width of spectrometer was set to 2 ms. The detector was set to 1.5 μs delay time between the laser pulse in order to prevent the detection of bremsstrahlung radiation.

2.2. Slag samples and LIBS measurements

A total of 20 slag samples were prepared by mixing six different reagents(CaO, SiO_2, Al_2O_3, MgO, TiO_2 and Fe_2O_3) according to two standard samples(open-hearth furnace slag(GSBH42011-94) and high titanium slag(YS/T 298-2007)). All of the six reagents were analytical pure reagent. Each slag sample was homogenized to produce a very fine powder until all of the powder passed through a 200-mesh stainless steel sieve using a ball grinding mill. Table 1 lists the concentration(wt. %) of major component of 20 slag samples(1-10# for open-hearth furnace slag, and 11-20# for high titanium slag). The slag sample is compressed a pellet to avoid laser scattering and benefit for collecting LIBS spectra. The slag pellet was made with a tablet press at 400 Mpa for 5 min. LIBS spectra of 20 different position of each sample surface are gathered. In order to decrease the effects of shot to shot fluctuations, each measure spectrum was obtained by accumulation of 50 laser pulses. The total of the spectra for 20 slag sample was 400(20 LIBS spectra for each slag sample). The data processing, classification and quantitative analysis for slag samples were completed on Matlab(2007a).

2.3. Support Vector Machines

Support vector machine(SVM) is a new and promising classification and regression method proposed by Vapnik.[22] It was originally developed for classification problems, but can also be extended to solve non-linear regression problems by means of ε-insensitive loss function. SVM method proposed is aimed at minimizing the structural risk rather than the empirical risk, and preserving a good generalization ability rather than optimizing the agreement with a given (limited) training set.

For a given training set A= $\{(x_1, y_1), (x_2, y_2), \ldots, (x_n, y_n)\}$, where each x_i is the input spectrum and has a corresponding target value or class label y_i for i =1, 2,..., n, where n refers to the number of the training samples. The concentration of major component from unknown slag sample can be predicted by the multivariate regression function $f(x)$ based on A. The complete SVM equations are summarized as follows[22]:

$$f(x) = \sum_{i,j=1}^{n} (\alpha_i - \alpha_i^*)(\Phi(x_i) \cdot \Phi(y_i)) + b \qquad (1)$$

Where α_i and α_i^* are the Lagrange multipliers satisfying the constraint $\alpha_i \geq 0$, $\alpha_i^* \leq C$. C is an additional parameter called the penalty error which determines the trade-off between the training error and model simplicity. The higher the value of C the more complex the boundary, and the more closely it fits samples, hence the lower the number of samples outside the margins. An infinite value of C tries to fit all samples inside the margins.

Table 1 The concentration(wt %) of major component in slag samples

No. sample	Fe_2O_3	SiO_2	TiO_2	CaO	MgO	MnO_2	Al_2O_3
1#	19.66	20.22	0.72	20.56	20.14	12.35	6.35
2#	16.15	17.90	0.40	23.15	21.27	14.27	6.86
3#	16.28	18.53	0.43	27.81	17.66	13.11	6.18
4#	17.64	18.71	1.06	24.61	15.68	15.12	7.18
5#	18.97	16.68	0.84	23.17	16.69	15.85	7.80
6#	20.06	19.99	0.53	22.93	17.62	12.84	6.03
7#	20.88	18.71	0.56	24.53	14.82	13.51	6.99
8#	19.86	16.41	0.65	26.77	17.17	12.90	6.24
9#	19.76	18.41	0.74	25.14	16.12	12.40	7.43
10#	18.84	18.22	0.78	25.03	16.92	14.18	6.03
11#	4.18	2.92	83.87	0.77	2.72	1.57	3.97
12#	4.53	2.92	84.32	0.57	3.02	1.11	3.53
13#	4.81	2.12	85.02	0.48	2.52	1.31	3.74
14#	4.82	2.82	84.74	0.43	2.72	1.07	3.40
15#	4.41	2.32	85.57	0.44	2.71	1.26	3.29
16#	3.44	3.05	85.44	0.60	3.05	1.08	3.34
17#	2.90	3.11	85.80	0.68	2.81	1.20	3.51
18#	4.35	3.17	83.83	0.74	2.87	1.29	3.76
19#	5.98	4.20	81.57	0.62	2.67	1.24	3.72
20#	3.62	2.51	85.44	0.62	2.99	1.45	3.38

The validity of the optimum model is tested in the prediction step, where an unknown $\hat{c}$ value can be obtained as follows:

For linear SVR prediction

$$\hat{c} = \sum_{i=1}^{n} (\alpha_i - \alpha_i^*) x_i' x_i + b \quad (2)$$

While, for nonlinear SVR prediction(i.e., using the kernel functions):

$$\hat{c} = \sum_{i=1}^{n} (\alpha_i - \alpha_i^*) K(x_i, y_i) + b \quad (3)$$

In support vector regression, All SVM models in our present study were implemented using the shareware program LibSVM developed by Lin[25]. The radial basis function(RBF) was used as kernel function in this work. For RBF kernel, the most important parameter is the width of the radial basis function. In addition, in order to evaluate the performance of the model to achieve quantitative and classification of slag, the root-mean-square error(RMSE) was calculated. The definition that we adopted for RMSE is given by

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{N} (\hat{y}_i - y_i)^2}{N}} \quad (4)$$

Where $\hat{y}_i$ corresponds to the reference value of concentration of the sample i, y_i is the value predicted by SVM, and N is the number of samples.

2.4. Partial least squares-discrimination analysis(PLS-DA)

PLS-DA is a multivariate inverse least-squares discrimination method used to classify samples based on a classical PLS regression, which provides a multivariate linear model for the relationship between a set of prediction variables and a set of response variables. The first step of PLS is to transform input variables into latent variables (LVs) in order to minimize the error. In the case of PLS-DA, the response variable is expressed by class membership. Then the PLS predicts the class number for each sample where the rotation of the LVs is focused on class separation.

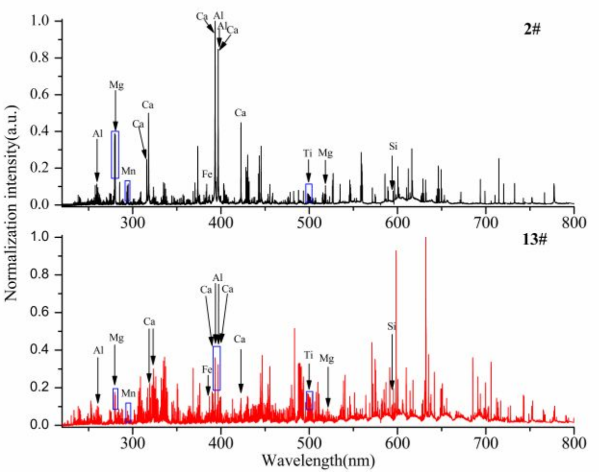

Fig. 1 LIBS spectrum of 2#(open-hearth furnace slag) and 13#(high titanium slag)

The sensitivity, specificity and accuracy are the statistical parameters to evaluate the performance of PLS-DA model for slag samples. The sensitivity is the percentage of the samples of a category accepted by the class model. The specificity is the percentage of the samples of the categories which are different from the modeled one, rejected by the class model. The accuracy of classification procedure is expressed as fraction of correctly classified samples to the total samples. [26]

3. Results and discussion

3.1. LIBS spectra and spectral normalization

Fig 1 shows the averaged normalization(by the maximum spectral intensity) spectrum of 2# and 13# slag sample in the range of 220-800nm, which includes the emission lines of the major component in slag. Slag is complex sample containing many chemical elements and thus related to LIBS spectra characterized by hundreds of atomic lines. There are obvious difference between the averaged normalization LIBS spectrum of 2# and 13# slag sample, which contributes to the classification and identification of open-hearth furnace slag and high titanium slag. The biggest different between open-hearth furnace slag and high titanium slag comes from the concentration of TiO_2, the concentration(wt %) of TiO_2 for open-hearth furnace slag is less 1.00%, moreover, the concentration(wt %) of TiO_2 for high titanium slag is over 80.00%. Spectral lines of major element(Ca, Si, Al, Mg, Fe, Mn and Ti) in slag sample were detected and identified based on NIST atomic database.[27] Some of the stronger elemental emission lines used for quantitative and classification analysis of slag sample were listed in Table 2. There are relative rich for Fe emission lines in slags, and spectral intensity of Ca, Si, Al, Mg and Ti were affected by matrix effect from slag samples and the rich iron emission lines.

3.2. Quantitative analysis of major component of slag

Quantitative analysis of major component of slag samples

Table 2 Some of the stronger element emission line for slag sample

element	spectral line/nm
Fe	278.81, 382.04, 385.99, 438.35
Si	288.15, 504.10, 594.85, 742.35
Ti	498.17, 499.11, 500.72, 501.42
Ca	315.98, 317.93, 393.37, 396.85
Mg	279.55, 280.27, 517.27, 518.36
Mn	279.48, 293.30, 293.93, 294.92
Al	257.51, 308.22, 309.27, 396.15

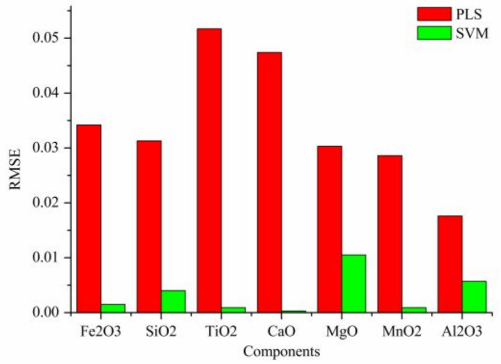

Fig. 2 The performance of PLS and SVM calibration model with 5-fold cross-validation

Table 3 The performance of PLS and SVM calibration model by 5-fold cross-validation with correlation coefficient(R^2)

Component	PLS	SVM
Fe_2O_3	0.8552	0.9994
SiO_2	0.8499	0.9984
TiO_2	0.9847	1.0000
CaO	0.9614	1.0000
MgO	0.8095	0.9840
MnO_2	0.7701	0.9982
Al_2O_3	0.7063	0.9819

plays a significant role to control quality and performance of steel products. Slags are complex samples containing many chemical elements and thus related to LIBS spectra characterized by hundreds of atomic lines. The whole spectra was selected as input valuable to complete the quantitative analysis of slag samples. In this work, the spectra for each slag sample was the average of 20 LIBS spectra from different positions. The total of the spectra for slag sample was 20, 16 samples(1-5#, 7-9#, 11-14#, 16-17# and 19-20#) were selected for the calibration the quantitative analysis(PLS and SVM) model, and the rest of samples(6#, 10#, 15# and 18#) were used for validation of the model.

Prior to construct the SVM calibration model, two significant parameter(kernel parameter of RBF-**γ** and **σ^2**) in SVM were optimized by GS approach with 5-folds CV in order to obtain the best performance of SVM calibration model. The optimized kernel parameter of RBF-**γ** and **σ^2** were 70 and 862. For the PLS model, the best latent variables(LV) optimized by 5-fold cross-validation is 8. Under the optimized SVM parameters and latent variables, the PLS and SVM calibration model was constructed using 16 training samples with the whole spectra as input variable. The predictive ability of PLS and SVM calibration model for slag sample was estimated by 5-folds CV. The RMSE and correlation coefficient(R^2) of major component in slag sample by PLS and SVM calibration model were shown in Fig 2 and Table 3. As we can see in Fig 2 and Table 3, the RMSE of major component in slag sample by SVM calibration model is obvious lower than by PLS calibration model; at the same time, the R^2 of major component in slag sample by SVM calibration model is obvious lager than by PLS calibration model. Hence, the SVM calibration model for slag sample shows a better performance than PLS calibration model.

Table 4 The prediction performance of PLS and SVM for slag sample

Component	PLS		SVM	
	Correlation coefficient($R^{2)}$	RMSE	Correlation coefficient($R^{2)}$	RMSE
Fe_2O_3	0.7597	0.0631	0.9521	0.0243
SiO_2	0.8237	0.0526	0.9099	0.0310
TiO_2	0.9848	0.1356	0.9919	0.0783
CaO	0.7207	0.1424	0.9652	0.0622
MgO	0.8740	0.0420	0.8816	0.0394
MnO_2	0.7635	0.0305	0.8642	0.0156
Al_2O_3	0.8874	0.0218	0.7699	0.0665

In order to validate the predictive abilities of SVM calibration model of slag sample, we compared SVM method with PLS method. Based upon the cross-validation results for all two models, SVM has a better predictive performance than the PLS models for slag samples. Table 4 lists the prediction performance of slag samples with PLS and SVM model. The SVM model was able to predict the concentration of major component in slag sample. As we can see in Table 4, there is a good linear relationship between the predictive value and the reference value of major component in test samples, and the R^2 of seven component in slag sample is lager than R^2 for PLS. Because the concentrations of TiO_2 and CaO are greater than other components in slag, the TiO_2 and CaO for test slag samples shows the best linear relationship. The concentration of Al_2O_3 in slag is relative low; therefore, the quantitative analysis result was affected by strong spectral lines from other elements and the matrix effect. The quantitative analysis of major component in slag sample is helpful for the classification analysis of different slags.

3.3. Identification and classification of two type of slag sample

Identification and classification of slag samples contributes to distinguish the quality and performance of steel product. It was fulfilled depend on difference of the component and correspond concentration of slag. In other words, identification and classification of slag sample was conformed by the difference comes from spectra integrated intensity and wavelength of slag LIBS spectra. Open-hearth furnace slag and high titanium slag were investigated in this work, and their major component were CaO, SiO_2, Al_2O_3, MgO, Fe_2O_3, MnO_2 and TiO_2.

Table 5 The performance of PLS-DA training model with different input variable by 5-folds cross-validation

Input variable	Latent variable	Sensitivity	Specificity	Accuracy	Cost time(s)
the full spectra	2	0.9986	1.0000	0.9993	11.26
the full normalized	3	0.9928	1.0000	0.9964	10.64
the first four more intensity emission lines	1	1.0000	1.0000	1.0000	2.51

The number of slag samples was 20, and 20 spectra was recorded for each slag sample. The total of LIBS spectral for slag samples is 400. The training set and test set were selected by Kennard-Stone algorithm[28,29] with the ratio of the number of train samples to the whole data is 0.7. The number of training samples(i.e. LIBS spectra, 14 spectra of 20 spectra for each slag sample was used for training sample) is 280, and the number of test samples is 120.

In PLS-DA, the latent variables are the number of lower dimensions onto which both the predictor and response variables are projected, and are generated to maximize the variance between each sample class. Identifying the variables that contribute the most to the separation of classes in the model ensures that the separation is attributable to the physical or chemical properties of the underlying system. The optimal number of LV for each PLS-DA model is determined by the point at which increasing the number of LV incorporates noise and other non-relevant information into the fit. Including too many LV could lead to overfitting in the model; overfitting can be avoided by testing the model with additional sample spectra not used to train the model[30].

The performance of PLS-DA training model was investigated by 5-fold CV with different input variables(the whole LIBS spectra without normalization, the full LIBS spectra with normalized by maximum spectral intensity, the first four more intensity emission lines of major component). The first four more intensity emission line of major components in slags was shown in Table 2. In 5-fold CV, the origin LIBS dataset is divided into five subsets. The holdout method is repeated five times, each time using one distinct set for testing and remaining four sets for training. The performance of PLS-DA training model with different input variable is shown in Table 5. As seen as Table 5, the sensitivity, specificity and accuracy of slag sample are the largest(1.0000) when the input variable is the first four more intensity emission lines of major component, and it takes less time(2.51 s). Hence, the first four more intensity emission lines of major component was selected as input variables to construct the PLS-DA training model for slags.

Based upon the cross-validation results for PLS-DA models, PLS-DA model with the first four more intensity emission lines of major component as input variable has a better identification and classification performance than with other input variable for slag samples. Hence, the PLS-DA model with the first four more intensity emission lines of major component as input variable was used to predict the external test set. Table 6 and Fig 3 show the classification results of PLS-DA training model for slags. In Fig 3, 1 and -1 stands for the high titanium slag and open-hearth furnace slag, respectively. Open-hearth furnace slag can be classified completely by PLS-DA training model. The classification accuracy of high titanium slag is 96.67%, this is possible because the some component of slag is similar and not easy to be distinguished. The nearly component, variations in the sample surface and instruct variability will cause difficulties.

Table 6 The classification results of PLS-DA training model for slags

Slags	Classification accuracy(%)	Misclassified ratio
Open-hearth furnace slag	100	--
high titanium slag	96.67	3.33

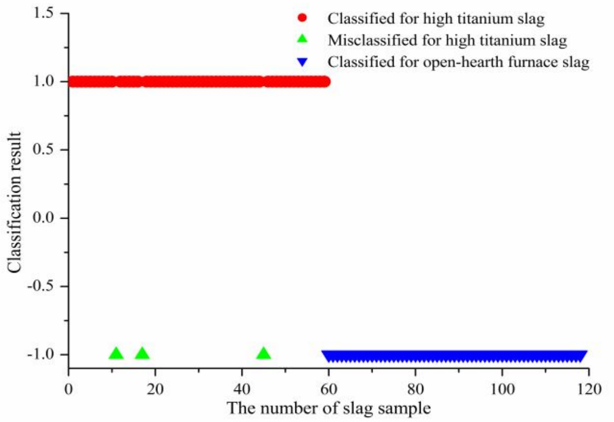

Fig. 3 The classification results with PLS-DA for slag samples

Conclusions

LIBS technique coupled with support vector machine(SVM) and partial least square(PLS) methods has been successfully used for the quantitative and classification analysis of 20 slag samples. The characteristic line (Ca, Si, Al, Mg and Ti) of LIBS spectra for slag samples can be identified based on NIST database. At first, quantitative analysis of the major components(Fe_2O_3, CaO, SiO_2, Al_2O_3, MgO and TiO_2) in slag samples were completed by SVM with the whole spectra as input variable, and the optimized kernel parameter of RBF-γ and σ^2 of SVM based on grid search approach were 70 and 862. The performance of SVM calibration model was investigated by 5-fold CV, the averaged prediction accuracy and root mean square error(RMSE) of SVM and PLS were calculated to validate the predictive ability of multivariate SVM calibration model in slag. SVM model can eliminate the influence of nonlinear factors dues to self-absorption in the plasma and provide a better predictive result. And then, two type of slag samples(open-hearth furnace slag and high titanium slag) were identified and classified by PLS-DA method with different input variables, sensitivity, specificity and accuracy were calculated to evaluate the classification performance of PLS-DA model for slag samples. Open-hearth furnace slag can be classified completely by PLS-DA training model and the classification accuracy of high titanium slag is 96.67%. It confirms that LIBS technique coupled with SVM and PLS methods is promising approach to achieve the online analysis and process control of slag and even metallurgy field.

Acknowledgments

Authors are thankful to the National Major Scientific Instruments and Equipment Development Projects of China(No. 2011YQ030113), National Natural Science Foundation of China (No. 21375105), Research Fund for the Doctoral Program of Higher Education of China (No. 20126101110019) and Scientific Research Plan Projects of Shaanxi Education Department(No. 14JK1746).

Notes and references

[a] *Institute of Analytical Science, School of Chemistry & Material Science, Northwest University, Xi'an 710069, P. R. China. Fax: Tel:86-29-88302635; E-mail: huali@nwu.edu.cn*
[b] *College of Science, Chang'an University, Xi'an, 710064, P. R. China*
[c] *School of Chemistry & Material Science, Northwest University, Xi'an 710069, P. R. China.*

1 H. Bennet, G. Oliver, *Minerals and Allied Materials,* John Wiley and Sons, New York, 1992.
2 S. M Jung, II Sohnb, D J Min, *X-Ray Spectrometry,* 2010, **39**, 311-317
3 L Marjanovic, R I. McCrindle, B M. Botha, H J. Potgieter, *Analtical and Bioanalytical Chemistry*, 2004, **379**, 104-107
4 S. Leroy, R. Simon, L. Bertrand, A. Williams, E. Foya and Ph. Dillmanna, *Journal of Analytical Atomic Spectrometry*, 2011, **26**, 1078-1087
5 B. Praher, R. Rössler, E. Arenholz, J. Heitz, J. D. Pedarnig, *Analtical and Bioanalytical Chemistry*, 2011, **400**, 3367-3375
6 M. P. Coustures, D. Béziat, and F. Tollon, *Archaeometry,* 2003, **45**, 599-613
7 D. A. Cremers, R. C. Chinni. *Applied Spectroscopy Reviews*, 2009, **44**, 457-506.
8 F. J. Fortes, J. J. Laserna. *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2010, **65**, 975-990.
9 D. W. Hahn, N. Omenetto. *Applied Spectroscopy*, 2012, **66**, 347-419.
10 S. J. J. Tsai, S. Y. Chen, Y. S. Chung, P. C. Tseng, *Analytical Chemistry*, 2006, **78**, 7432-7439.
11 L. M. Cabalín, A. González, J. Ruiz, J. J. Laserna, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2010, **65**, 680-687.
12 R. Noll, V. Sturm, U. Aydin, D. Eilers, C. Gehlen, M. Höhne, A. Lamott, J. Makowe, J. Vrenegor, *Spectrochimica Acta Part B- Atomic Spectroscopy*, 2008, **63**, 1159-1166.
14 D. L. Death, A. P. Cunningham and L. J. Pollard, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2008, **63**, 763-769.
15 P. Yaroshchyk, D. L. Death and S. J. Spencer, *Journal of Analytical Atomic Spectrometry*, 2012, **27**, 92-98.
16 R. Noll, H. Bette, A. Brysch, M. Kraushaar, I. Monch, L. Peter and V. Sturm, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2001, **56**, 637-649.
17 L. Peter, V. Sturm and R. Noll, *Applied Optics*, 2003, **42**, 6199-6204.
18 M. A. Gondal, T. Hussain, Z. H. Yamani and A. H. Bakry, *Journal of Environmental Science and Health Part A- Toxic/Hazardous Substances and Environmental Engineering*, 2007, **42**, 767-775.
19 M Kraushaar, R Noll, H. U. Schmitz, *Applied Spectroscopy*, 2003, **57**, 1282-1287.
20 V. Sturm, H. U. Schmitz, T. Reuter, R. Fleige, R. Noll, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2008, **63**, 1167-1170.
21 B. Praher, R. Rössler, E. Arenholz, J. Heitz, J. D. Pedarnig, *Analtical and Bioanalytical Chemistry*, 2011, **400**, 3367-3375.
22 B. Praher, V. Palleschi, R. Viskup, J. Heitz, J.D. Pedarnig, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2010, **65**, 671-679.
22 L. Xu, V. Bulatov, V. V. Gridin, I. Schechter, *Analytical Chemistry,* 1997, **69**, 2103-2108.
23 V. Vapnik, *Statistical Learning Theory*,Wiley, New York, 1998.
24 T. Zhang, L. Liang, K. Wang, H. Tang, X. Yang, Y. Duan and H. Li, *Journal of Analytical Atomic Spectrometry*, 2014, **29**, 2323-2329
25 C. C. Chang and C. J. Lin, *LIBSVM-A Library for Support Vector Machines*, http://www.csie.ntu.edu.tw/~cjlin /libsvm/.
26 V. K. Unnikrishnan, K. S. Choudhari, Suresh D. Kulkarni, Rajesh Nayak, V. B. Kartha and C. Santhosh*, RSC Advances,* 2013, **3**, 25872-25880
27 A. Kramida, Yu. Ralchenko, J. Reader, NIST ASD Team, NIST Atomic Spectra Database (ver. 5.0), [online], National Institute of Standards and Technology, Gaithersburg, MD, 2012. (Available: http://physics.nist.gov/asd).
28 R. W. Kennard, L. A. Stone, *Technometrics*, 1969, **11**, 137-149.
29 E. Bouveresse, C. Hartmann, D. L. Massart, I. R. Last, K. A. Prebble, Analytical Chemistry. 1996, **68**, 982-990.
30 J. J. Remus, J. L. Gottfried, R. S. Harmon, A. Draucker, D. Baron and R. Yohe, *Apply Optics*, 2010, **49**, C120-C131