

Comparison of Calibration Curve Method and Partial Least Square Method in the Laser Induced Breakdown Spectroscopy Quantitative Analysis

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Received August 2013

ABSTRACT

The Laser Induced Breakdown Spectroscopy (LIBS) is a fast, non-contact, no sample preparation analytic technology; it is very suitable for on-line analysis of alloy composition. In the copper smelting industry, analysis and control of the copper alloy concentration affect the quality of the products greatly, so LIBS is an efficient quantitative analysis technology in the copper smelting industry. But for the lead brass, the components of Pb, Al and Ni elements are very low and the atomic emission lines are easily submerged under copper complex characteristic spectral lines because of the matrix effects. So it is difficult to get the online quantitative result of these important elements. In this paper, both the partial least squares (PLS) method and the calibration curve (CC) method are used to quantitatively analyze the laser induced breakdown spectroscopy data which is obtained from the standard lead brass alloy samples. Both the major and trace elements were quantitatively analyzed. By comparing the two results of the different calibration method, some useful results were obtained: both for major and trace elements, the PLS method was better than the CC method in quantitative analysis. And the regression coefficient of PLS method is compared with the original spectral data with background interference to explain the advantage of the PLS method in the LIBS quantitative analysis. Results proved that the PLS method used in laser induced breakdown spectroscopy was suitable for simultaneous quantitative analysis of different content elements in copper smelting industry.

Keywords: Laser-Induced Breakdown Spectroscopy (LIBS); Partial Least Square Method (PLS); Matrix Effects; Quantitative Analysis

1. Introduction

In the field of metallurgical industry, current and the conventional analysis methods are chemical analysis, spark atomic emission spectrometry, flame atomic absorption spectrometry and so on. These methods require the sample pretreatment and analysis process is more complex, thus increasing the metallurgical production time and causing a great deal of energy and material waste. Laser Induced Breakdown Spectroscopy (LIBS) is an emission spectrum analysis technology which uses a pulse laser as the energy source and both qualitative and quantitative analysis of elements can be achieved [1,2]. It is a fast, noncontact, no sample preparation analysis technology and becomes a hot topic in the field of spectral analysis in recent years [3-5]. In the copper smelting industry, the lead brass has excellent cutting performance, wear resistance and high strength, and it is widely used in valve,

lock, clock and watch manufacturing industry. But the lead brass is a complex copper alloy composed of a variety of elements. It has two main content elements Cu and Zn. Meanwhile the Ni, Al, Pb, Sn elements have a decisive role to its heat resistance, corrosion resistance, strength and ductility. The concentrations of main content elements and other elements differed by several orders of magnitude cause a great matrix effects. So as the conventional LIBS quantitative analysis method, the Calibration Curve (CC) method has the poor accuracy.

Partial least squares (PLS) is a set of multivariate linear regression (MLR) and principal component regression (PCR) basic functions method. It is a pattern recognition method that has powerful processing ability of high dimension data. It has been widely used in the biomedical, pharmaceutical, social science and other fields [6-8]. In this paper, the PLS method was used to overcome the multiple correlations between variables of the spectroscopic data and lead brass LIBS complex spectra

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were quantitatively analyzed. PLS method was compared with the traditional calibration curve(CC) method to verify the superiority in the LIBS quantitative analysis.

2. Experiment

The experimental device set is shown in the **Figure 1**. The ND: YAG laser made by BigSky Company is plasma excitation source, the output wavelength is 1064 nm, the maximum output energy is 200 mJ. The pulse laser produced plasma at the sample surface through a 75 mm focal lens. Detection device is composed of 4 piece of Ocean Optics company HR2000+ spectrometer, the optical resolution of 0.1 nm (FWHM), the integration time is 1ms, the measurement wavelength range is 199 - 631 nm. The timing controller is made by us to control Q delay of laser device and delay between spectrometer and laser device, the Q delay range is 120 μ s - 220 μ s, adjustable step is 5 μ s, spectral acquisition delay range is 0 μ s - 10 μ s, adjustable step is 0.1 μ s. The analyzed lead brass sample is spectral purity Chinese standard sample; the GB number is GSB 04-2416-2008. The Composition is shown on the "Ref. (Reference) line" in **Table 1**.

In this experiment, the laser pulse energy is 95 mJ, pulse frequency is 10 Hz. The spectral acquisition delay is 2.4 μ s to eliminate the background noise caused by bremsstrahlung in the early stage of plasma [9]. Each sample was measured 10 times in 5 different locations separately, in order to prevent the error caused by inhomogeneous in its internal composition. Before the data collection, there are 10 excitation pulses for ablation the

surface of the sample to clean the oxide impurities. There is not any pretreatment process in the whole experiment. The LIBS data of 6 samples is 300. Each sample data is 50, 40 of them used to establish the quantitative calibration model, the other 10 data for prediction to validate the performance of quantitative methods.

3. Result and Discussion

3.1. Calibration Curve (CC) Method

The experimental spectral data is shown in **Figure 2**. Most characteristic spectral lines are in the range 200 - 300 nm. Access to the National Institute of Standards and Technology (NIST) atomic emission spectrum database, the higher intensity and can be resolved element spectral peaks is : Cu 324.754 nm, Pb 280.1995 nm, Al 257.5094 nm, Ni 221.6482 nm. These characteristic spectral lines are used for calibration curve (CC) method quantitative analysis.

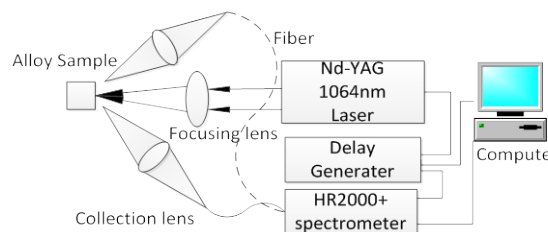


Figure 1. Schematic diagram of the LIBS experimental setup.

Table 1. Predicted VS. Reference concentration (wt%) of all elements By PLS and CC method.

No.		Cu	Pb	Ni	Al
	Ref.	59.98	0.414	1.474	0.075
1	PLS Pre.(M \pm SD)	60.09 \pm 0.22	0.418 \pm 0.085	1.449 \pm 0.065	0.076 \pm 0.069
	CC Cal.(M \pm SD)	59.72 \pm 1.03	0.11 \pm 0.089	1.141 \pm 0.158	0.198 \pm 0.023
	Ref.	57.77	0.76	0.795	0.0116
2	PLS Pre.(M \pm SD)	58.03 \pm 0.22	0.874 \pm 0.088	0.849 \pm 0.067	0.081 \pm 0.071
	CC Cal.(M \pm SD)	59.39 \pm 1.49	0.472 \pm 0.138	0.353 \pm 0.253	0.02 \pm 0.003
	Ref.	57.09	1.421	0.347	0.177
3	PLS Pre.(M \pm SD)	57.25 \pm 0.22	1.442 \pm 0.088	0.369 \pm 0.067	0.236 \pm 0.0715
	CC Cal.(M \pm SD)	56.73 \pm 0.84	1.222 \pm 0.234	0.137 \pm 0.125	0.013 \pm 0.0814
	Ref.	58.64	1.81	0.104	0.452
4	PLS Pre.(M \pm SD)	59.02 \pm 0.23	1.869 \pm 0.092	0.196 \pm 0.07	0.519 \pm 0.075
	CC Cal.(M \pm SD)	61.27 \pm 2.12	1.498 \pm 0.261	0.021 \pm 0.072	0.956 \pm 0.183
	Ref.	58.76	2.405	0.0286	0.761
5	PLS Pre.(M \pm SD)	58.56 \pm 0.20	2.292 \pm 0.081	0.073 \pm 0.062	0.706 \pm 0.065
	CC Cal.(M \pm SD)	59.49 \pm 1.38	2.914 \pm 0.268	0.32 \pm 0.049	1.463 \pm 0.142
	Ref.	59.6	1.393	0.386	0.262
6	PLS Pre.(M \pm SD)	59.60 \pm 0.23	1.476 \pm 0.089	0.479 \pm 0.068	0.375 \pm 0.0731
	CC Cal.(M \pm SD)	58.79 \pm 1.46	1.967 \pm 0.318	0.189 \pm 0.092	0.151 \pm 0.101

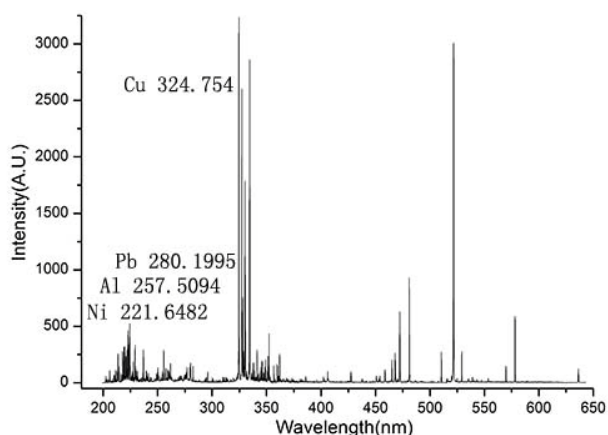


Figure 2. The LIBS spectrum of lead brass.

The calibration curve of element Pb on the characteristic spectral line 280.2 nm is shown in **Figure 3**. The star symbols in the figure represent the relationship between concentration and average intensity of characteristic spectral line. The vertical lines between the circle symbols represent the standard deviation of the calibration data. Calibration model is linear fitting and the correlation coefficient “R” is 0.9776. The remaining 60 spectral data are measured by this model.

Similarly, the other elements calibration curves and measured data can be obtained by the same way. The concentration measured of elements Cu, Pb, Ni and Al is shown on the “CC Cal. ($M \pm SD$) line” in **Table 1**. The correlation coefficient R of calibration curve for Cu (280.1995 nm) is 0.9176, for Ni (221.6482 nm) is 0.9687, and for Al (257.5094 nm) is 0.9446. The concentration result shows that calibration curves method for lead brass quantitative analysis is not good. That is because the concentration of lead brass are complex, the main element Cu content is only about 60%, there are severe matrix effects in the other elements measurement. Meanwhile the lead brass texture is very soft, which means the laser ablation quality is different from each other every time. So the result stability is also not good.

3.2. Partial Least Squares (PLS) Method

Using the same experimental data, quantitative analysis was performed by partial least squares method. The independent variable is the LIBS spectral data obtained from the experiment, from 199 to 631 nm there are totally 7895 spectral data points, namely there are 7895 dimensions, the modeling data number is 240. The dependent variable is the concentration of 4 elements, so there are 4 dimensions. The dependent variable is a multidimensional matrix, so the model we used is PLS2 model. The full cross-validation method is used to validate the model. The detailed regression and verification method can be

reference literature about multivariate data analysis [10, 11].

In the PLS method, Selection of the number of Principal Components (PC) depends on the residual Y variance value in calibration model. The residual variance shows the discrete degree of residual. With the increase number of Principal Components, the Y residuals discrete degree becomes lower. But much more numbers of PC make the model more complex, and more systematic noise will be introduced. So when the number of PC increases, while the residual Y variance does not decrease obviously, the number of PC is the most suitable for the model. **Figure 4** shows the relationship between Residual Y-variance and PCs of experimental data. When the number of PC is 7, the residual Y variance is 0.0317, this value is very small and residual Y variance does not decrease significantly as it increases. So the number of PC of the PLS2 model is 7.

The relationship between predicted concentration and reference concentration of element Pb by PLS2 model is shown in the **Figure 5**. The correlation coefficient “R” is 0.9902, Root Mean Square Error of Prediction (RMSEP) is 0.0911. In this model, the correlation coefficient “R” between predicted concentration and reference concentration of Cu is 0.9667, Ni is 0.9885, Al is 0.9554. The result of predicted concentration is shown on the “PLS Pre. ($M \pm SD$) line” in **Table 1**. The PLS method results and correlation coefficients showed very well.

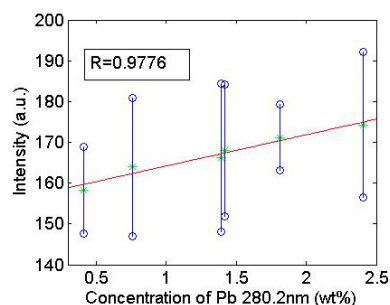


Figure 3. Calibration curve of element Pb on line 280.2 nm.

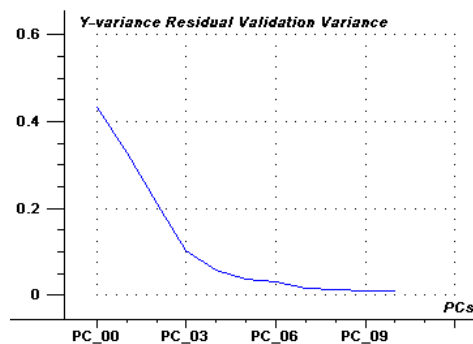


Figure 4. Residual Y-variance VS. PCs.

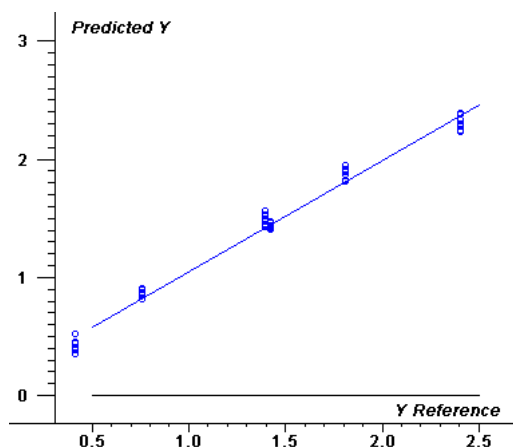


Figure 5. Predicted VS. Reference concentration (wt%) of Pb.

3.3. The Advantage of PLS Method

In PLS method, the regression coefficient means the relationship between all independent variable X and dependent variable Y, it can be calculated in the corresponding number of principal components. In Section 3.2, independent variable X (LIBS spectra data) and dependent variable Y (element concentration) are used to establish the PLS calibration model. The regression coefficient between spectra data and element concentration of Al is shown in the **Figure 6**. The dark line of **Figure 6** means the regression coefficient with ordinate on the right side, the light line means the spectra intensity with ordinate on the left side. The spectral wavelength range is 350 - 400 nm in the **Figure 6**. It can be observed that at wavelength 394.25 nm and 396.06 nm, the regression coefficient is 1.82×10^{-4} and 2.99×10^{-4} , that is a larger value. It means at this wavelength, the element concentration and the spectra data have great correlation in PLS model. Access to NIST, line 394.4 nm and 396.15 nm is the Al characteristic spectral line. So in PLS model, independent variables and dependent variables have great correlation at element characteristic spectral line (small differences between the above wavelengths are caused by error of spectrometer). But the intensity of spectra at the same wavelength is weak and unstable. So the CC method calibration model using single spectral line intensity is not good enough.

At wavelength 352.29 nm there is a peak but not Al characteristic spectral line, it does not work in the CC method Al calibration model. The regression coefficient at the same wavelength is -0.92×10^{-4} , it means the spectral intensity and Al concentration are negative correlation at this wavelength in PLS method calibration model.

Unlike CC method to select the individual characteristic peak, PLS method is to establish the relationship be-

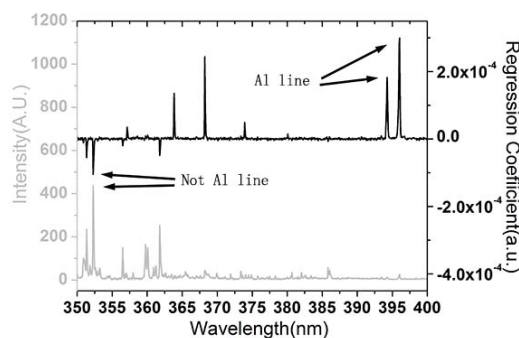


Figure 6. The regression coefficient and spectrum of Al.

tween the intensity of full spectrum and element concentration. By changing the independent variable space to build a new principal components coordinate system, PLS method establish positive or negative correlation relationship between all the spectral line intensity and element concentrations. Then by selecting the number of principal components to reduce the dimension of raw data, PLS method establish a more stable quantitative calibration model. We believe that this is the reason why PLS quantitative calibration model is more effective than CC method.

4. Conclusion

In this paper, both partial least squares and the calibration curve method were used to make the quantitative analysis of LIBS spectral data of lead brass. After establishing the PLS calibration model, we can quickly get the results of all the elements concentration. Compared with the CC method, PLS method is more suitable for the complicated matrix, element content different alloy.

5. Acknowledgements

This work has been supported by the Equipment Development Programs of the Chinese Academy of Sciences (Grant No. YZ201247), the National High-Tech Research and Development Program of China (863 Program) (Grant No. 2012AA040608) and the National Natural Science Fund (Grant No. 61004131).

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