In situ analysis of steel melt by double-pulse laser-induced breakdown spectroscopy with a Cassegrain telescope

Lanxiang Sun a,b,*, Haibin Yu a,b, Zhibo Cong a,b, Yong Xin a,b, Yang Li a,b, Lifeng Qi a,b

a Shenyang Institute of Automation, Chinese Academy of Sciences, Shenyang 110016, China
b CAS Key Laboratory of Networked Control Systems, Shenyang 110016, China

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A B S T R A C T

A laser-induced breakdown spectroscopy (LIBS) system combining a Cassegrain telescope and a double-pulse laser mode was developed for the in situ analysis of steel melt. Optical- and electrical-related devices were sealed in an enclosed box away from the high-temperature steel melt surface. Connected to the box by a flange, a long hollow steel tube was used for the laser and plasma emission transmission path. At the tip of the steel tube, a refractory lance that can withstand high temperatures was immersed into the molten steel surface to pass through the surface slag layer. The designed optical structure successfully keeps the photoelectric-associated system components away from the high-temperature environment, thus reducing the complexity of system protection and maintenance. The signals obtained from single-pulse and double-pulse LIBS were comprehensively compared; the effect of argon blowing on spectral stability was analyzed; and the quantitative analysis of Si, Mn, Cr, Ni and V in molten steel samples was evaluated using both a univariate model and a partial least squares (PLS) model. The relative root mean square error of prediction (RMSEP) values and average relative standard deviations (RSDs) of the PLS model were approximately 5% and 2%, respectively, both of which are less than those of the univariate calibration model. The sealed LIBS setup was also transferred to a steel plant for application testing, and the obtained accuracy approached the plant’s accuracy requirements. Furthermore, quantitative analysis of carbon was also achieved on the basis of the PLS models. These results demonstrate that the developed system is promising for the in situ analysis of melt steel in the steelmaking industry.

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1. Introduction

In the metallurgical industry, in situ analysis of the chemical elemental components in the metal smelting process is a significant requirement for process control and quality assurance. At present, the conventional techniques used for elemental analysis in steelmaking plants are still off-line methods that require solidified samples to be transported to an adjacent laboratory for analysis. Common measurement methods such as spark source optical emission spectrometry (Spark-OES), X-ray fluorescence (XRF) spectrometry and inductively coupled plasma optical emission spectrometry (ICP-OES) are not easily applied to real-time and in situ analysis because of the need for sample pre-treatment [1]. Under optimum conditions, the total time required for analysis, including the sample pre-treatment time, is still greater than 3 min.

Laser-induced breakdown spectroscopy (LIBS) is a versatile analysis technique for many types of materials [2–6]. In LIBS, light emitted from plasma induced by focusing high-power laser pulses onto the sample surface is collected for spectral analysis. Because no sample pre-treatment is required and because of its versatile analysis of solids, liquids and gases, LIBS is most suitable for in situ and stand-off measurements [7]. In the metallurgical industry, LIBS can be used to perform in situ monitoring of melt composition during production, which is one of the most interesting and promising areas of LIBS research [8–17].

Carlhoff and Kirchhoff [18] were the first to apply LIBS for the in situ analysis of molten steel in a converter. Aragón et al. [19] also reported a melt-steel analysis method involving LIBS, in which the laser beam was focused onto a free melt surface from above, resulting in a precision of 10% for carbon content analysis in the concentration range 150–1100 ppm. Noll et al. [13,20] developed a LIBS system for the on-line measurement of molten steel composition by using a model lance consisting of a vacuum optical probe, a permanent lance and a lance tip immersed into the liquid steel melt; using this system, light elements including C, P and S were successfully quantified directly in a molten steel bath. Gruber et al. [21] studied changes in the LIBS signal induced by adding admixtures containing elemental Cr, Cu, Mn, and Ni in a laboratory induction furnace. In this setup, the LIBS signal was carried by a 12-m fiber-optic bundle to the spectrometer. These authors later developed a portable LIBS system for the rapid on-line analysis of
liquid steel in two different vacuum furnaces [22]. Hubmer et al. [10] proposed a method for analyzing liquid high-alloy steel using a fiber-optic cable to carry the signal over a distance of approximately 10 m. The analyzed elements included Cr, Ni, Mo, Cu, and Co, and the obtained errors were less than 0.2 wt.% in the concentration range below 24.4 wt.%.

Palanco et al. [11] described an open-path and remote LIBS system with a 7.5-m beam path. A laboratory-scale induction furnace with a 1 kg capacity was used for the tests, and the changes in content of Cr and Ni were successfully monitored. Victor et al. [23] successfully adopted a Newton telescope to continuously monitor changes in Si and Mn in blast-furnace runners. Sun et al. [24–26] developed an open-path LIBS system for monitoring compositional changes in Cr, Mn, Si and Ni in a 30 kg capacity induction furnace and demonstrated that the detection capability of minor elements in molten steel is greater than in solid normal steel.

Although the literature contains numerous such studies on melt metal measurements using LIBS, applying LIBS in an active steelmaking process remains a challenge. The probes used in LIBS setups for melt measurements can broadly be divided into two styles: those in which the probe is immersed in the melt surface and those in which a telescope structure is adopted to execute open-path measurements. In the case of the immersion-style probes, long-term protection and maintenance of the probes is one of the greatest challenges to their widespread adoption. In the case of the open-path style, the serious influence of surface slag on measurements is unavoidable.

The Fraunhofer-Institut für Lasertechnik (ILT) designed an automatic liquid slag LIBS analyzer that consists of an optical module connected by
a nitrogen-purged steel tube (length ≈ 3.5 m) on the bottom [27,28]. Because the tube contains no optical units and the core parts of the system are kept several meters from the high-temperature slag, the complexity of system protection and implementation is reduced. This LIBS analyzer was successfully tested at a steelworks for three months.

In the present work, we developed a LIBS system with a structure similar to that of ILT’s slag analyzer for the in situ analysis of steel melt. In this system, double-pulse LIBS and a Cassegrain telescope structure are combined in an immersion-style setup. A several-meter gas-purged steel tube is used, the tip of which is connected to a refractory lance that is immersed in the liquid surface to avoid surface slag influence when executing measurements. To improve the long-distance signal, a double-pulse LIBS mode was also adopted in the system. Using double or multiple pulses separated by a short delay time (several microseconds) can produce a lower LOD and significant enhancements of emission line intensity as well as much improved signal-to-noise ratios [29–35]. However, to the best of our knowledge, the effect of double- or multi-pulses on steel melt has not been previously studied.

The signals obtained from single-pulse and double-pulse LIBS are comprehensively compared, the effect of argon blowing on spectral stability is analyzed and the quantitative analysis of molten steel samples using univariate models and PLS models is evaluated in this work. Furthermore, after testing in the laboratory, the system was transferred to a steel plant for application tests; the test results are also discussed in the following text.

2. Methods and experiments

The structure of the LIBS system developed for the in situ analysis of molten metal is shown in Fig. 1(a). Most optical-related components are sealed in the integrated optical box. The two laser power units, spectrometer, time-delay controller and the step-motor controller outside the integrated optical box are sealed in the outside box. Spectral and control signals are transmitted to a remote computer by an Ethernet cable. A stainless steel tube connected to the integrated optical box by a flange is used to transmit laser and plasma emissions. A refractory lance joined to the tip of the steel tube can be immersed into the molten steel to pass through the surface slag layer. Argon is blown through the steel tube and the refractory lance to disperse some smoke and slag on the melt surface.

Experiments and tests were successively conducted in our laboratory and in a steel plant. In our laboratory, an induction furnace with a 1 kg capacity was used to smelt steel; a photo of the setup taken during an experiment is shown in Fig. 1(b). At the steel plant, the sealed LIBS setup was installed along the ladle path. In the steelmaking process at this steel plant, the steel is first smelted in 40 ton converters, and the molten steel is subsequently poured into ladles to implement the alloying process to control the quantity of Mn, Si and other components. Sampling and analysis are necessary steps in the alloying process, requiring an approximately five-minute waiting time. During the waiting time, we operated the LIBS system to perform a measurement process that only needs approximately 1 min and does not disturb the production process. Fig. 2 shows photos of the application testing setup. The dimensions of the outside sealed box are 980 × 750 × 1300 mm³ and the weight is approximately 370 kg. When starting the measurement process, the sealed system and argon-purged tube were lowered until the lance tip

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Content (%)</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>V</th>
<th>Fe</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td></td>
<td>0.010</td>
<td>0.130</td>
<td>0.020</td>
<td>0.020</td>
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<td>0.526</td>
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<td>0.833</td>
<td>0.057</td>
<td>96.69</td>
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<td>3</td>
<td></td>
<td>0.405</td>
<td>0.318</td>
<td>1.234</td>
<td>1.041</td>
<td>0.072</td>
<td>96.12</td>
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<tr>
<td>4</td>
<td></td>
<td>0.282</td>
<td>0.527</td>
<td>1.832</td>
<td>1.134</td>
<td>0.089</td>
<td>95.33</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>0.663</td>
<td>0.982</td>
<td>2.426</td>
<td>1.392</td>
<td>0.255</td>
<td>93.47</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>0.852</td>
<td>1.192</td>
<td>3.363</td>
<td>3.361</td>
<td>0.430</td>
<td>90.01</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>1.223</td>
<td>1.666</td>
<td>4.753</td>
<td>4.770</td>
<td>0.669</td>
<td>86.17</td>
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<tr>
<td>8</td>
<td></td>
<td>1.392</td>
<td>1.960</td>
<td>6.269</td>
<td>6.790</td>
<td>0.752</td>
<td>82.11</td>
</tr>
</tbody>
</table>

Fig. 3. Schematic of the integrated optical system.

Fig. 4. Single-pulse and double-pulse spectral comparison for melt and solid steel samples.
was immersed into the liquid steel surface to a depth of approximately 25 cm. When adequate data had been obtained, the system was elevated to a certain height to await the measurement of another ladle.

The distance from the glass window of the optical box to the tip of the refractory lance was approximately 2.8 m in the laboratory and 4.5 m in the steel plant; the length of the refractory lances were 300 mm and 800 mm; and the lances’ inner diameters were 18 mm and 40 mm, respectively.

A schematic of the integrated optical box is shown in Fig. 3. Two pulsed Nd:YAG lasers (Litron NANO SG120 and SG150, with a wavelength of 1064 nm, pulse width of 6–8 ns, spot diameter of 4–5 mm, and max repetition frequencies of 20 and 10 Hz, respectively) are combined by a combination optical system comprising half-wave plates and polarization beam splitters (PBSs). The combined beams are reflected to a fivefold Galilean laser focusing system through mirror 1 and mirror 2. After the focusing system, the laser beam is reflected by mirror 3 and mirror 4, then passes through the glass window to be focused on the distant sample surface, thus stimulating the sample to generate plasma. The laser focusing system can adjust the laser focus from distances ranging from 1 to 10 m by changing the distance between the two groups of lenses. The photodiode (Thorlabs, DET10A) can monitor the energy of the two lasers in real time.

Plasma emission light is collected through a Cassegrain telescope system in which the diameter of the primary mirror is 160 mm and the diameter of the secondary mirror is 40 mm. Collected light is coupled to a spectrometer (Ocean Optics HR2000+, with wavelengths of approximately 185–327.7 nm and an approximate resolution of 0.15 nm) by a fiber-optic cable. In fact, the real obtained spectral range is above 230 nm because lines below 230 nm are completely attenuated in such a long open path. The secondary mirror of the telescope system can be driven by a stepping motor to adjust the distance between the primary and secondary mirrors to achieve the best collecting effect.

In the initial stages of plasma formation, because of the influence of bremsstrahlung and free-bound electronic recombination continuum radiation, the spectrum has a low SNR. Changing the delay time between the pulses and the spectrometer can efficiently improve the SNR. In the experiment, the delay time between the two lasers, the spectrometer gate delay time after the second laser pulse and the integral time of the spectrometer were optimally set to 3 μs, 2.5 μs and 1 ms, respectively.

In our laboratory, eight different steel alloy samples were sequentially smelted in the furnace for testing. For each sample, more than 500 spectra were acquired with a 10 Hz shot frequency. The chemical compositions of the samples are listed in Table 1.

### 3. Results and discussion

#### 3.1. Comparison of single-pulse and double-pulse spectra

To compare the single-pulse and double-pulse spectra under the same conditions, the laser pulse energy at the sample surface was set near the maximal value of 65 mJ in single-pulse mode and both laser pulse energies were also set to 65 mJ in double-pulse mode. Under these settings, the laser energy in double-pulse mode was twice that in single-pulse mode. We did not perform experiments in which the sum of the double-pulse energy was equal to the single-pulse energy because our purpose was to obtain the largest SNR using the existing equipment. Fig. 4 shows a comparison of single-pulse and double-pulse spectra of sample 3.

The double-pulse enhancement effect of liquid steel samples is obviously lower than that of solid steel samples; for example, the signal intensity of the Fe I line at 281.3 nm is approximately 7 times greater in double-pulse mode than in single-pulse mode for solid samples, but is only 2.8 times greater for liquid samples.

A Boltzmann plot was constructed using some characteristic Fe lines to identify the cause of the differences in the enhancement effect, as shown in Fig. 5. The plasma temperatures for four different cases were calculated as follows: \[ T(\text{single, solid}) = 10,384 \pm 674 \text{ K}, \]
\[ T(\text{double, solid}) = 11,176 \pm 740 \text{ K}, \]
\[ T(\text{single, liquid}) = 11,128 \pm 640 \text{ K}, \]
\[ T(\text{double, liquid}) = 11,425 \pm 716 \text{ K}. \]

The determination coefficients \((R^2)\) were 0.940, 0.938, 0.953 and 0.944, respectively.

The plasma temperature was approximately 800 K higher in double-pulse mode than in single-pulse mode for solid steel samples, but approximately 300 K higher for liquid steel samples. The plasma temperature apparently reaches a certain degree of saturation in double-pulse mode for liquid steel samples; thus, the plasma temperature is insensitive to the laser energy. At the same time, the plasma
temperature in double-pulse mode for solid samples approaches the plasma temperature in single-pulse mode for liquid samples.

The signal enhancement of plasma in double-pulse mode is mainly caused by an increase of the plasma temperature or an increase of the plasma particle number density [32,35]. Because the plasma temperatures in the four cases do not vary greatly, the signal enhancement in double-pulse mode is mainly due to increased plasma particle number density under these experimental conditions. A higher ablation rate is reasonably expected when the temperatures of solid steel samples approach their melting points because the thermal mobility of both electrons and atoms is highly enhanced [11,36]. Therefore, the particle density of plasma induced from high-temperature samples should be greatly improved compared with that induced from normal-temperature samples. For the solid steel samples in double-pulse mode, the first laser beam changes the state of the sample surface and increases the temperature of the sample surface. The second laser beam then passes through the plasma, couples to the high-temperature sample surface, and thus generates denser particles. The enhancement effect is therefore significant in this case. For the liquid steel samples in double-pulse mode, because the temperature of the liquid samples is already sufficiently high, the first laser beam can also stimulate more particles compared to the normal solid samples; thus, the enhancement effect is not as obvious as in the solid samples.

In addition to enhancing the signal intensity, double-pulse mode can also reduce fluctuations in spectral line intensity to a certain extent. Fig. 6 shows a comparison of the fluctuations in the single-pulse and double-pulse modes for all molten steel samples. The relative standard deviation (RSD) was calculated using one hundred relative intensity ratios between the Si line at 288.16 nm and the Fe line at 281.3 nm, and one hundred relative intensity ratios between the Mn line at 293.3 nm and the Fe line at 281.3 nm. Good repeatability was achieved for both single-pulse and double-pulse modes. The RSDs were all less than 4% in both single-pulse and double-pulse mode, except in the case of sample 2. In particular, the RSDs in double-pulse mode were less than 2% for most samples, which is considerably lower than the RSDs in single-pulse mode. This result indicates that the plasma induced from liquid steel samples is more stable, which is perhaps due to several reasons. First, the matrix effect of liquid steel samples is less than that of solid steel samples because the consistency of liquid metal is more uniform than that of solid metal. Second, as in the aforementioned analysis, the plasma temperature reaches a certain saturation value and is then no longer sensitive to the laser energy, especially in double-pulse mode. Furthermore, although the enhancement of plasma temperature is not obvious, the second pulse can further atomize particles that were not atomized by the first laser pulse, thereby making the plasma temperature more uniform.

### Table 2
Calibration results for univariate models.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analytical lines/reference lines (nm)</td>
<td>Si 288.16/Fe 281.3</td>
<td>Mn II 293.3/Fe 281.3</td>
<td>Cr II 286.67/Fe 281.3</td>
<td>Ni I 305.4/Fe 281.3</td>
<td>V II 311.07/Fe 281.3</td>
</tr>
<tr>
<td>R²</td>
<td>0.974</td>
<td>0.989</td>
<td>0.987</td>
<td>0.984</td>
<td>0.986</td>
</tr>
<tr>
<td>RMSE (%)</td>
<td>0.077</td>
<td>0.073</td>
<td>0.24</td>
<td>0.27</td>
<td>0.047</td>
</tr>
<tr>
<td>LOD (ppm)</td>
<td>107</td>
<td>134</td>
<td>649</td>
<td>430</td>
<td>88</td>
</tr>
</tbody>
</table>
is completely unnecessary because the fluctuations can be suppressed through the use of an internal standard.

3.3. Quantitative analysis

Two calibration methods were compared: one is the univariate calibration model, and the other is the PLS model. Only 8 different samples were used in this laboratory experiment. Because of the limited number of experimental samples and to test how the equipment endures repeated use, the experiment for each sample was repeated twice. In this manner, after the first experiment on a sample was completed, the lance was lifted out of the surface and then immersed again for the second experiment. The data acquired in the first experiment were used for calibration, and the second set of experimental data was used for prediction. A total of 200 spectra were used for analysis in each experiment. The 200 spectra were divided into 20 groups with 10 spectra per group, and the average of 10 spectral values in each group was considered as 1 measurement point. This procedure is equivalent to 20 repeated measurements. This method of group division is very important for improving a PLS model. In this way, defects in a small number of samples can be remedied to a certain degree, and the repeatability of predictions can be improved. The selected spectral section used as input ranged from 277.81 nm to 327.743 nm, corresponding to pixels from 1301 to 2048, or 748 variables. Because the spectral line intensity is weak and spectral interference is high at wavelengths below 277.81 nm, spectral values below 277.81 nm were not incorporated into the model. Moreover, the selected spectral section, which already covers rich spectral lines of the analyzed elements, can provide sufficient information for analysis.

The univariate calibration results are shown in Table 2, where the calibration models are linear for Si and Mn but quadratic for Cr, Ni, and V. The calibration curves for Si and Cr are shown in Fig. 8. The determination coefficients ($R^2$) of the calibration curves were all greater than 0.98, except for that of the calibration curve for Si ($R^2 = 0.974$). The RMSE is the average root-mean-square error of the 8 samples. The RMSE and LOD values for Cr and Ni were higher than those for the other elements, mainly because the concentrations of these two elements exceeded by 6.2% and because the selected spectral lines used for calibration are not resonance lines. If the composition of low-concentration Cr and Ni is to be analyzed, the LOD can be reduced by selecting the elements’ resonance lines. Thus, the LOD of these elements is estimated to be on the order of 100 ppm, and the concentration prediction error is expected to be less than 0.1% at a concentration of approximately 1%. We did not obtain an LOD of the same order of magnitude as that obtained by Noll et al. [13,20], mainly because of the limitations of the detector used in our experiments and the long optical distance.

PLS is a useful multivariate method that utilizes abundant spectral information to compensate for different deviations [37]. For PLS calibration models, sample 3 and sample 7 were used for testing; the other 6 samples were used for calibration. A total of 20 data points from each sample were introduced as input variables, and, although only 6 concentrations were used for each element, this data processing approach simulated an experiment comprising $20 \times 6 = 120$ samples.
The determination coefficients between the reference and the predicted concentrations were all greater than 0.99, which was considerably better than the results of the univariate calibration. The relative curves for the reference and predicted concentrations of Si and Cr are shown in Fig. 9, in which circles denote the calibration samples and asterisks denote the test samples.

Data from the second experiment of 7 samples were used for predictions based on the established calibration models; the predicted concentrations are shown in Fig. 10. Sample 1 is not included in the prediction because of its extremely low elemental concentrations. The average of the results of 10 shots was used as a measurement value, and 20 measurement values correspond to 1 sample. The upper curves are the results predicted on the basis of the PLS models, and the lower curves are the result based on the univariate calibration models. The RMSE of prediction (RMSEP) and mean standard deviation (MSD) of the predictions were calculated; the results are shown in Table 3. MSD denotes the mean of the standard deviations of 20 measurement values for the 7 samples. RMSEP and MSD represent accuracy and repeatability, respectively.

From Table 3, the RMSEP and MSD of PLS models were both less than those of the univariate calibration models. When the content was less than 1%, the RMSEP was mostly less than 0.05%; when the content was greater than 1%, the RMSEP was mostly less than 0.2%. In general, the relative RMSEP was approximately 5%. In addition, the concentration predictions exhibited good repeatability, given that the average
relative standard deviation (RSD) was between 2% and 3%, excluding some outliers. These results from the in situ analysis are very exciting. Under a limited experimental situation in which a small number of calibration samples were used, constructing PLS models with multiple data points from one sample was effective.

3.4. Steel plant tests

After laboratory testing, the sealed LIBS setup was transferred to a steel plant for application testing on Sep. 25, 2014. After more than two months of system debugging and improvements in the steel plant, we completed the calibrations and performed in situ measurements on steel melt. Reference calibration values were obtained from the steel plant laboratory, where the standard Spark-OES was used to analyze the samples. The steel compositions measured by Spark-OES were used for calibration and validation are shown in Table 4, in which the first 10 samples were used for calibration and the subsequent 5 samples were used for validation.

We wanted to use as few reference samples as possible for calibration because a facile calibration process is important for the practical application of this method. As in the above proposed PLS processing method, we used 10 reference samples from different ladles for calibration, but only tens of useful spectra were obtained from each ladle after abnormal data were rejected because of the limited immersion time. These spectral data were divided into several groups with 10 spectra for each group, and the average value of each group was considered as 1 measurement datum point. Several measurements from each sample were introduced as input variables, and, although fewer than 10 concentration values were used for each element (given that elemental concentration in different ladles was the same), this data processing approach approximated 43 calibration samples.

Because we were limited to the steel types made by this steel plant, only three elements — C, Si and Mn — were analyzed; their calibration curves and test results are shown in Fig. 11. Using the calibration curves, we tested another 5 samples from 5 different ladles; these results are also included in Fig. 11. Adopting the same data processing method for the calibration, there were 18 test values in all (shown with "*" in Fig. 11). For the three elements, the linear fits of the Spark-OES reference values vs. the measured LIBS values yielded an almost ideal line $y = x$ with a determination correlation $R^2$ of 0.978 for C, 0.986 for Si, and 0.988 for Mn; the RMSEPs of the three elements were 0.015%, 0.029% and 0.062%, respectively. Although serious interferences are present in steel plants, such as vibrations, unstable surfaces and variations in immersion depth, the obtained accuracy approached the steel plant’s requirements. Furthermore, we used the PLS method to quantitatively analyze C even though its valid analytical lines could not be detected and other analytical lines such as that at 247.86 nm could not be resolved. We have previously demonstrated that taking advantage of the PLS method enables the C component of solid steels to be quantified [38], and the results obtained here demonstrate that PLS is also applicable to liquid steels.

### Table 4

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>C (wt%)</th>
<th>Si (wt%)</th>
<th>Mn (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.25</td>
<td>0.62</td>
<td>1.31</td>
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<tr>
<td>2</td>
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<tr>
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</tr>
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<td>15</td>
<td>0.21</td>
<td>0.55</td>
<td>1.25</td>
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4. Conclusions

A double-pulse LIBS system was developed for the in situ analysis of molten steel and other high-temperature liquids. In this system, which comprises a Cassegrain telescope and a long hollow steel tube, optical- and electrical-related devices are sealed in an enclosed box away from the high-temperature melt steel surface. At the tip of the steel tube, a refractory lance is immersed into the molten steel surface to pass through the surface slag layer. The complexity of system protection and maintenance is greatly reduced by the system’s long-distance optical structure.

The signals obtained from single-pulse and double-pulse LIBS for liquid and solid steel samples were comprehensively compared. The signal enhancement in double-pulse mode is mainly due to the increased plasma particle number density. In addition to enhancing the signal intensity, double-pulse mode can also reduce fluctuations in the signal’s spectral line intensity.

The effect of blowing argon through the tube was analyzed. Blowing argon did cause large fluctuations in the net spectral intensity, but such fluctuations can be mitigated by using the normalized relative intensity. Therefore, an internal standard element and internal lines are necessary to achieve good repeatability.

Two types of calibration models, the univariate calibration model and the PLS model, were used for the quantitative analysis of elemental components in molten steel samples. The accuracy and repeatability of PLS models were both better than those of the univariate calibration models. Based on PLS models, the relative RMSEP values were approximately 5%, and the average RSDs were between 2% and 3%.

The sealed LIBS setup was also transferred to a steel plant for application testing. Although the results were not as good as those obtained in a laboratory setting, the obtained accuracy approached the steel plant’s requirements. Furthermore, we used the PLS method to quantitatively analyze C even though its valid analytical lines could not be resolved. These obtained results demonstrate that the developed...
LBS system is promising for the in situ analysis of melt steel in the steelmaking industry.

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