Calibration transfer method for the quantitative analysis of high-temperature materials with stand-off laser-induced breakdown spectroscopy

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This work reports on the capabilities of stand-off LIBS to perform quantitative analysis in materials at high temperature. Long distance analysis is essential to avoid risk for the operator and the instrument. Characterization of the ablation regime at high sample temperature has been carried out by determining the average ablation rate and the plasma electron temperature and electron density. Boundary conditions for the applicability of the method are reported and its suitability is demonstrated for the quantitative analysis of Cr, Ni and Mn in stainless steel samples at 1000 °C. An analytical method to transfer results from hot samples to a room temperature calibration was developed. This method avoids the need to perform a calibration procedure at high temperature and is based on a linear transformation of the high-temperature results to their low-temperature counterparts.

Introduction

In the metallurgical industry, conventional methods of analytical control entail an excessive time cost, since the sample must be transported to the laboratory, prepared and analyzed before critical decisions based on the analytical results are taken. When analyzing liquid steel, sampling entails a serious risk to the operator since this operation is performed at scarcely three meters from the converter. It seems, therefore, reasonable that any attempt to perform an on-site analysis of hot steel should be preferably directed under a remote configuration basis free of sampling risks and preparation delays. As an alternative, laser-ablation based techniques combine several advantages for this type of in-process control since they deliver rapid analytical results without sample preparation. Among these techniques, laser-induced breakdown spectroscopy (LIBS) is a suitable tool due to its multielemental capability for the analysis of solids, liquids and gas samples.\(^1\)\(^2\)\(^3\) LIBS can provide qualitative and quantitative information in real time and in an industrial environment.\(^6\)\(^7\)\(^8\) The possibility of stand-off elemental analysis is unique to remote LIBS revealing the technique as an appealing tool for the analysis of inaccessible samples or those for which proximity entails a risk for the operator and/or the instrument. In recent years, several publications have reported the development,\(^9\)\(^10\)\(^11\)\(^12\) and applications\(^4\)\(^5\)\(^6\)\(^7\)\(^8\) of remote LIBS. However, the ablation process largely depends on sample temperature, in such a way that a calibration curve at high temperatures is unique to remote LIBS revealing the technique as an appealing tool for the analysis of inaccessible samples or those for which proximity entails a risk for the operator and/or the instrument.

In a previous work,\(^16\) an alternative method for direct measurements of composition in samples at high temperature was developed. This method uses a transfer function which allows one to obtain the composition of the sample at high temperature using a calibration curve performed with standards at room temperature, thus avoiding the need to perform calibration curves at high temperatures. The suitability of using the transfer method for the analysis of slags was demonstrated. The present work provides an insight into the fundamentals of this transfer method in conjunction with remote LIBS for the determination of composition of steel samples at high temperature. Boundary conditions for the applicability of the transformation method have been identified and demonstrated with theoretical calculations. Knowledge of plasma parameters, such as the mass ablated and the electron temperature, proved necessary for use of the method. As an example of its suitability for in-process steel analysis at high temperature, the composition of Ni, Cr and Mn in eight different stainless steel samples was measured at 1000 °C with a room temperature calibration. The correlation achieved between these results and the determination at room temperature was close to unity.

Experimental

The system used for this application has been already described in a former paper,\(^16\) where the experimental setup is sketched showing the components of the remote LIBS system. The laser was a Q-switched Nd:YAG (1064 nm) operating at 10 Hz in its fundamental wavelength. The pulse width, beam diameter and maximum energy provided by the laser were 12 ns, 12 mm and 1500 mJ, respectively. The experimental setup used for this application, was set in a coaxial configuration,\(^12\) allowing the laser beam and the returning plasma light to share the same optical path. The beam was focused at a stand-off distance of 12 m by means of a 8.9× beam expander composed by a couple of antireflection coated best form BK7 lenses. By moving the distance between these two lenses, the focus was adjusted along the optical path to generate a plasma at different distances from the laser. This feature provides the possibility of analysis with a wide depth of focus at remote distances. The couple of lenses were moved by means of a PC-controlled micrometric stage to ensure the accuracy at the modification of the focus distance. The emission light was collected by a 300 mm diameter aluminium flat mirror, tilted 45° from the laser axis. This mirror was drilled in the centre with a 110 mm hole to allow the laser beam to pass through this aperture without physical restrictions. The light collected was projected to a Newton telescope with F/4 and a primary mirror of 200 mm in diameter that focused the plasma light to a 600 μm fibre optic cable (fused silica, NA 0.22). A couple of plane-convex lenses matching the F/# of the fibre optic cable and the spectograph were used to couple the plasma light to the latter (Acton Research Inc., f = 275 mm, F/3.9). A 1800 grooves mm\(^{-1}\) grating was used to disperse the plasma light entering in the...
spectrograph, and an intensified CCD camera (1024 × 128 pixel CCD fitted with a 18 mm intensifier) was used as a detector. The acquisition conditions were controlled by a pulse and delay generator (Stanford Research Systems) and were fixed to 0.8 μs and 15 μs in delay from the laser pulse and integration time, respectively.

Samples
Fifteen steel standards containing a wide concentration range of Fe, Cr, Ni and Mn were used to elaborate the calibration plots. The measurements were carried out at room temperature, keeping the samples in a holder located at 12 m distance from the instrument. The second part of the work was carried out measuring eight steel samples (1N500, 2B800, 3B800, 4A57, 5R54 F1, 3T72 F2, 5X28 F2, 2Z31) at temperatures ranging from 25 °C to 1000 °C. Table 1 summarizes the composition as measured by Spark-OES of the samples used in the experiment. The samples were placed inside an oven for some minutes before firing the laser in order to avoid the temperature gradients in the sample during the first seconds of the heating. The oven was kept open to allow optical access of the beam while the laser was being fired during 50 s (500 shots for each sample). The drop of sample temperature when the oven was opened was not significant. After each sample analysis, the temperature was restored keeping the oven closed for 5 min.

The spectral region between 372 nm and 406 nm was chosen for this work, due to the presence of Fe, Cr, Ni and Mn emission lines with low spectral interferences. Fig. 1 shows the spectral window and the main spectral lines chosen to perform the analytical calculations.

Results and discussion
Plasmas generated with laser pulses in the order of the nanoseconds are mainly produced through inverse bremsstrahlung absorption processes while those generated with laser pulses shorter than the 50 ps are thought to be produced through multiphoton ionization. Assuming local thermodynamic equilibrium (LTE) conditions, the Boltzmann equation predicts an increase in signal emission, I, via a raise in the ablated mass, M, and/or by an increase in the plasma temperature, T;

\[ I_a = M C_a \left( \frac{g_i A_i h \nu / c^2}{Z_a e} \right) \]

where \( I_a \) is the weight fraction of species \( z \) in the plasma, \( g_i \) is the statistical weight of the upper electronic level, \( A_{kl} \) is the transition probability from level \( k \) to \( i \), \( Z_a \) is the partition function of species \( z \) while \( h \), \( k \) and \( c \) are the Planck constant, the Boltzmann constant and the speed of light constant, respectively. Besides plasma temperature, another important parameter influencing the intensity of emission is sample temperature. Its effect on plasma emission intensity has been formerly reported, evidencing the dependence of the ablation rate and thus, of the plasma atomic emission on sample temperature when using nanosecond laser pulses. The influence of sample temperature and of the ablation rate on line emission has been studied measuring the emission intensity of several atomic lines as well as the ablated mass of stainless steel samples at temperatures rising from 25 to 1000 °C. Above 1000 °C, some difficulties in the crater depth measurement come up due to the formation of a posterior detachment of an oxide layer on the sample surface owing to the destruction of the anticorrosive Cr2O3 layer by chemical reaction in oxygen and water vapor environment at high temperature. Samples were shot on five different positions with 200 cleaning laser pulses and 300 acquisition pulses. The crater sizes were measured with an optical microscope. Fig. 2 shows the behavior of the average ablation rate (AAR) versus the temperature of the sample. As illustrated, the mass removed increases with the sample temperature. Owing to the formation of mentioned layer, the precision in the results is poorer at high temperatures. This fact can be observed in Fig. 2, where the higher SDs were obtained at higher sample temperatures. The need of a higher amount of cleaning laser shots previous to the acquisition in order to drill the oxidation layer increases with temperature.

![Fig. 1](image1.png)

**Fig. 1** Spectral window showing emission of the elements of interest in a stainless steel sample. The spectrum was acquired at 12 m and is the average of 100 laser shots at 10 Hz.

![Fig. 2](image2.png)

**Fig. 2** Variation of the averaged ablation rate (AAR) with sample temperature. Each point is the average of the result obtained for 5 measurements. The inset illustrates the variation of the AAR as a percentage of that obtained at room temperature with sample temperature.

**Table 1** Chemical composition of the steel standards

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
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<tr>
<td>1N50</td>
<td>66.06</td>
<td>15.74</td>
<td>0.16</td>
<td>0.14</td>
</tr>
<tr>
<td>2B80</td>
<td>62.32</td>
<td>21.75</td>
<td>14.75</td>
<td>0.08</td>
</tr>
<tr>
<td>3B80</td>
<td>61.18</td>
<td>18.96</td>
<td>15.17</td>
<td>0.04</td>
</tr>
<tr>
<td>4A57</td>
<td>67.45</td>
<td>16.73</td>
<td>11.07</td>
<td>0.29</td>
</tr>
<tr>
<td>5R54</td>
<td>82.85</td>
<td>16.17</td>
<td>0.13</td>
<td>1.58</td>
</tr>
<tr>
<td>3T72</td>
<td>70.70</td>
<td>18.19</td>
<td>8.22</td>
<td>1.88</td>
</tr>
<tr>
<td>5X28</td>
<td>70.51</td>
<td>18.19</td>
<td>8.08</td>
<td>1.76</td>
</tr>
<tr>
<td>2Z31</td>
<td>67.46</td>
<td>16.78</td>
<td>11.29</td>
<td>1.31</td>
</tr>
</tbody>
</table>

Fixed to 0.8 m and delay generator (Stanford Research Systems) and were measured with an optical microscope. Fig. 2 shows the behavior of the average ablation rate (AAR) versus the temperature of the sample. As illustrated, the mass removed increases with the sample temperature. Owing to the formation of mentioned layer, the precision in the results is poorer at high temperatures. This fact can be observed in Fig. 2, where the higher SDs were obtained at higher sample temperatures. The need of a higher amount of cleaning laser shots previous to the acquisition in order to drill the oxidation layer increases with temperature.

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The inset in Fig. 2 illustrates the variation percentage of the AAR with sample temperature compared with that obtained at room temperature. This plot highlights the increase of the ablated mass at higher temperatures when compared with lower temperatures. As can be appreciated, an increase in AAR higher than 850% was reached at 1000 °C. This effect is indicative of a high dependence between the mass ablated and the spectral intensity.

The temperature of the plasma was calculated at several sample temperatures by using the Boltzmann plot method. The lines fulfilled the requirements of close wavelength proximity and significant differences in their upper energy levels. Fig. 3 presents the behavior of the electron temperature of the plasma versus the temperature of the sample. As shown, \( T_e \) increases with sample temperature, but this rise is not so abrupt as the ablation mass percentage. The inset in Fig. 3 illustrates the variation percentage of \( T_e \) with sample temperature compared to that obtained at 25 °C. An increase from 25 to 1000 °C in the sample temperature leads to a \( T_e \) increase close to a 14%. Thus, both variables, ablation rate and electron plasma temperature, are partly responsible for the variation of the emission intensity with sample temperature.

Selection of spectral lines

Emission spectroscopy for the measurement of sample composition at different temperature conditions requires selection of non-saturated spectral lines. Eqn (1) relates line intensity to the ablated mass and the electron temperature of the plasma. As mentioned in discussion of Fig. 2 and 3, there is an increase in the AAR and \( T_e \) with sample temperature and that leads one to expect an even higher density in the LIP for samples at high temperature, and therefore, a significant self absorption of the radiation within the plasma. In this sense, Fig. 4 shows the logarithm of the intensity-mass ratio for Fe(I) 374.95 nm and Mn(I) 403.01 nm emission lines versus \(-1/T_e\). As shown, the logarithm of the intensity-mass ratio follows a decreasing curve for Fe, while for Mn, the plot fits to a growing straight line (except for the last point which has been excluded from the linear fit). As can be seen in Fig. 1, the emission intensity for the Fe line is almost three times higher than that for Mn. This led to an early intensity saturation with sample temperature for the Fe line. Thus the selection of spectral lines must be done carefully and acquires special importance when applying the transfer method presented in this paper.

Transfer method

In a previous work, a method to transform the intensity, \( I_{HT} \) of a given line measured at high temperature (HT) to its corresponding intensity, \( I_{RT} \) at room temperature (RT) was presented. In this way, a calibration curve performed with standards at RT is useable for samples at HT just by transforming the signal of the element of interest measured at HT into its RT equivalent. The transfer function follows a linear transformation:

\[
I_{RT} = A_{HT} + B
\]

where \( A \) and \( B \) are two constants calculated from two measurements of the standards at each extreme of the calibration plot both at RT and at HT. Though this mathematical model has been widely used to recalibrate analytical systems that need periodical servicing, it has been adapted to a new situation where the sample conditions—sample temperature in this case—are different in the recalibration process. However, it has been empirically found that some boundary conditions must be obeyed for the model to work properly: (i) The emission response must remain equivalent both for the element of interest and the internal standard along the working temperature range. Emission intensities for Cr, Ni and Mn normalized to Fe emission line were studied for a temperature range from 25 to 1000 °C. The slope for each of the three species was close to zero (\(-6 \times 10^{-5}\) for Cr, \(1.6 \times 10^{-4}\) for Ni and \(9.9 \times 10^{-5}\) for Mn) being indicative that the emission response remains equivalent both for the element of interest and the internal standard in the whole range of studied temperatures. (ii) The calibration plot at HT must obey a straight line. The absence of a saturation effect in the curve of growth for samples at HT ensures the suitability of the linear transformation in order to produce an equivalent linear calibration plot at RT. Since the objective of the method is to avoid a whole HT calibration, a simplification can be done using the plots in Fig. 4 with a standard sample of the highest concentration of the element of interest. Linearity of the plot will guarantee the applicability of the method.

To demonstrate its potential, the method was applied to the quantitative analysis of the stainless steel samples described in Table 1. RT calibration plots were elaborated for Cr, Ni and Mn. Five measurements were performed on different positions of each standard. The lines used for normalization fulfilled requirements such as being associated with the same ionization state and having similar excitation energies. A summary of the lines selected as well as the analytical figures of merit are detailed in Table 2. As shown, linearity is highly satisfactory for the three elements. The correlation of Cr, Ni and Mn concentration determined by remote LIBS in samples at 1000 °C and then transferred to RT has been plotted in Fig. 5.
versus the values obtained for the same samples at RT. Fig. 5(a)–(c) show the correlation between the concentration for Cr, Ni and Mn determined at 1000°C using the transfer method and that obtained with RT LIBS from the same samples. As shown, there is an excellent correlation between results obtained with remote LIBS at HT and those obtained directly at RT. The accuracy of the method, represented by the slope of the three plots, is very close to unit for the three cases. Correlation coefficients and slope were respectively 0.9978 and 0.9946 for Cr, 0.9910 and 0.9996 for Ni, and 0.9112 and 1.0363 for Mn. Relative error percentage between the RT LIBS and the HT LIBS transferred was calculated for the three elements. Except for the lower concentration samples where the error made was higher than 50% (in 3B80 and 1N50 for the measurement of Mn and Ni errors, respectively), the remaining samples presented an acceptable accordance between RT LIBS and HT LIBS transferred values, with a relative error lower than 16%, 21% and 6% for Mn, Ni and Cr, respectively.

Conclusions

This work emphasizes the capabilities of stand-off LIBS to perform quantitative analysis in samples at high temperature. Characterization of the LIP and the ablation process has been carried out by determining the main plasma properties such as electron temperature, electron density and AAR. An analytical method has been presented to transfer results from hot samples to a room temperature calibration. This method is based on a mathematical model and avoids the need to perform a calibration procedure at high temperature via a linear transformation which transfers a room-temperature calibration plot to enable its use at high temperature. Boundary conditions for the applicability of the method have been identified and reported. The suitability of the method has been demonstrated with stainless steel samples at 1000°C and reflected in the figures of merit for Cr, Ni and Mn. The applicability of the method is not only restricted to metallurgical products but it could be readily extended to other materials provided that the described boundary conditions are fulfilled.

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References


**Table 2** Analytical figures of merit. CLR, calibrated linear range in weight percent of the calibrated element; $R$, correlation coefficient; BEC, background equivalent concentration

<table>
<thead>
<tr>
<th>Element of interest</th>
<th>Internal standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>$\lambda$/nm</td>
</tr>
<tr>
<td>Cr</td>
<td>379.66</td>
</tr>
<tr>
<td>Ni</td>
<td>377.56</td>
</tr>
<tr>
<td>Mn</td>
<td>403.01</td>
</tr>
</tbody>
</table>

**Fig. 5** Correlation between the concentration measured with remote LIBS at high temperature and using the transfer method versus the value obtained by remote LIBS at room temperature for Cr (a), Ni (b) and Mn (c).