Quantitative analysis of samples at high temperature with remote laser-induced breakdown spectrometry using a room-temperature calibration plot

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Abstract

A method for measurement of composition in samples at high temperature using a calibration curve performed at low temperature is presented. The method uses a transfer function which avoids the need for building a calibration plot at high temperature. The method has shown suitability for high-temperature measurements up to 850 °C in steel slags exhibiting coefficients of correlation of 0.991 and 0.989 for Si/Ca and Mg/Ca ratios, respectively. The accuracy of the method has been assessed by comparing the results with remote LIBS at high temperature to those by XRF at room temperature. As an example of its versatility, the method has been applied to the determination of the basicity index of steel slags at high temperature.

1. Introduction

The quality of a finished product largely depends on the possibility of having representative feedback in different fabrication stages. The analytical control of the pre-product along the fabrication process is essential, from the first treatments to the finished product. In metallurgical industry, conventional methods of analytical control entail an excessive time cost, since the sample must be transported to the laboratory and prepared for the analysis. In certain cases the high temperatures involved in the fabrication process entail a serious risk to the operator. The composition information about products or by-products has to be determined by conventional methods—XRF, Spark-OES, ICP-OES—being necessary to spend too much time waiting for sample cooling and preparation to proceed to the analysis.

It seems, therefore, reasonable that when high temperatures are involved, any attempt to perform the analytical control should be preferably directed under a contact-free configuration free of sampling risks and also of preparation delays. 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) has been already reported to provide qualitative and quantitative information in real time and under a variety of industrial environments [1–4]. Stand-off elemental analysis is unique to LIBS. Several publications have assessed the development [5–7] and applications [1,8–10] of the technique.

However, the high dependence of the laser ablation process on sample conditions would make necessary to follow a special procedure when building a calibration plot. This fact would entail to reproduce the same exact environment of the production samples—atmosphere and temperature—for the whole set of standards which, in addition, would be destroyed. This could be further complicated if the...
dimensions often involved in an industrial process are considered. All these drawbacks reveal the need for an analytical method capable to relate the intensity measurements at room temperature to those at high temperature.

In this work, an alternative method enabling to perform direct measurements of composition in samples at high temperature is demonstrated. This method uses a transfer function which allows obtaining 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. As an example of the suitability of the method for the determination of in-process parameters at high temperature, the basicity index of steel production slags samples at 850 °C has been measured in a laboratory muffle. Immediate benefits of room-temperature calibration for measurements with remote LIBS at high-temperature save time and, subsequently, costs.

2. Experimental

A remote LIBS instrument was used to analyze slag samples inside a laboratory muffle placed at 12 m from the instrument. Fig. 1 sketches the experimental layout showing the components of the remote LIBS system. A Q-switched Nd:YAG laser operating at 1064 nm provides pulses up to 1500 mJ and 12 ns in a flat spatial profile of 12 mm in diameter. The beam was focused at a stand-off distance using an 8.9× beam expander integrated by two 1064 nm antireflection-coated best-form BK7 lenses with effective focal lengths of −22.25 mm and 198.84 mm. The focal length can be adjusted by changing the distance between both lenses. To collect the returning light, several aspects have to be considered for the design of the system such as geometry, wavelength range, efficiency interfacing to spectrograph, size and cost. The geometry chosen for this work was a coaxial set-up, in which the laser beam and the plasma emission share the same optical axis. A flat mirror of 300 mm in diameter and tilted 45° to the laser beam is used to fold the returning light from the plasma to the telescope. The expanded and focused laser beam passes through a 110 mm diameter aperture drilled in the center of this mirror. A commercial Newton telescope with F/4 and a primary mirror of 200 mm in diameter was employed for light collection. This telescope focuses the plasma light to a 600 μm fiber optic cable (fused silica, NA=0.22). A couple of plano-convex lenses matching the F/# of the fiber optic cable and

<table>
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<th>Sample</th>
<th>F (%)</th>
<th>Na (%)</th>
<th>Mg (%)</th>
<th>Al (%)</th>
<th>P (%)</th>
<th>K (%)</th>
<th>Ca (%)</th>
<th>Si (%)</th>
<th>Cr (%)</th>
<th>Ti (%)</th>
<th>Mn (%)</th>
<th>Fe (%)</th>
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<td>0.10</td>
<td>8.15</td>
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<td>0.03</td>
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<td>0.02</td>
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<td>43.97</td>
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<tr>
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Fig. 1. Instrument setup. 1. laser source, 2. focusing beam expander, 3. circular-crown mirror, 4. Newton telescope, 5. spectrograph, 6. intensified CCD, 7. fiber optic, 8. coupling lenses, 9. computer.
the spectrograph were used to couple the plasma light to the latter (f = 275 mm, F/3.9, 1800 groove mm⁻¹ grating). An intensified CCD camera (1024 × 128 pixel CCD fitted with a 18 mm intensifier) was used as a detector. A laser repetition rate of 10 Hz was used and the acquisition conditions were fixed to 1 μs and 20 μs in delay from the laser pulse and integration time, respectively.

3. Samples

The samples employed in the present work were steel slag samples provided by Acerinox, S.A (Los Barrios, Cádiz, Spain) and exhibited different sizes and irregular shapes. Their composition as determined by X-ray fluorescence is summarized in Table 1.

4. Results and discussion

Fig. 2 shows a LIB spectrum acquired at 12 m from a steel slag sample at room temperature. Emission corresponding to Ca, Mg, Si and Cr is shown. The analysis conditions were optimized for the slag samples resulting in 50 preparation shots followed by 50 averaged spectra with five replicates for each sample. Calibration plots were built for Si(I) 288.16 nm and Mg(II) 279.55 nm both normalized to Ca(I) 300.68 nm. Table 2 summarizes the analytical figures of merit for each element. Ca(I) 300.68 nm proved to be a suitable internal standard for the emission lines chosen for Mg and Si, yielding straight lines with correlation coefficients close to one along each calibrated range.

4.1. Influence of sample temperature on laser ablation

The influence of sample temperature on the in-depth variation of signal intensity has been studied. For most samples, the intensity profile showed a stable plateau where intensity remains relatively constant for a given number of shots. The extent and average intensity of the plateau varies with sample temperature. The higher the sample temperature, the higher the average intensity of the plateau and the shorter its extent. An explanation to this behavior could rely either on the increase of the ablation rate at higher sample temperatures as well as in a possible raise of plasma temperature. Both effects have been observed before [1,8]. Beyond the mentioned plateau, all samples converge to a similar intensity value regardless of the starting temperature. As the laser ablates the sample and the crater is deeper, its walls can block the radial expansion of the plasma. When the crater depth is similar or larger than plasma dimensions, the shielding effect by plasma channeling increases, thus decreasing the fraction of pulse energy coupled to the sample. Consequently, the ablation rate and, in turn, the emission intensity reach a minimum [11,12].

4.2. High-temperature measurements

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

\[
I_{RT} = A \cdot I_{HT} + B
\]

where \( A \) and \( B \), are two parameters which are calculated from measurements of two samples at each extreme of the calibration plot. The analytical procedure requires to measure the intensity of a given element in a sample both at room temperature and at the process temperature where the calibration plot is to be transferred. Thus, obtaining a pair of values both for \( I_{RT} \) and for \( I_{HT} \) allows the calculation of \( A \) and \( B \).
and $B$ as summarized in Table 2 for Si/Ca and Mg/Ca ratios. 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. Fig. 3 shows the effect of sample temperature on Si(I) 288.16 nm and Mg(II) 279.55 nm signals normalized to Ca(I) 300.68 nm signal. Each point is the average of shots #50 to #99 for both elements. As shown, both plots exhibit a similar trend with a linear increase of the normalized signal with temperature up to approximately 850 °C. From this point a steeper slope is found and then an apparent saturation is noticed beyond 1000 °C. This effect is mostly due to Si and Mg emission as shown in the inset. Therefore, the maximum affordable temperature to apply the method to the slag samples is 850 °C. (ii) The calibration plot at high temperature must be a straight line. The absence of saturation effect in the curve of growth for samples at high temperature guarantees the applicability of the method. Thus, the concentration range has been restricted to that actually used in the steel making process rather than using a non linear wider range. To demonstrate the potential of the method, the correlation of the Si/Ca concentration ratio measured with remote LIBS in samples at 850 °C has been

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**Fig. 3.** Dependence on the sample temperature for Si(I) 288.16 nm and Mg(II) 279.55 nm signals normalized to Ca(I) 300.68 nm signal. The inset illustrates the individual contribution of each line as a function of sample temperature (■) Si(I) 288.16 nm, (○) Mg(II) 279.55 and (▲) Ca(I) 300.68 nm.

Fig. 4. Correlation between the Si/Ca concentration ratio measured by remote LIBS at high temperature and using the transfer method versus the nominal value as measured by XRF at room temperature.

Fig. 5. Correlation of the basicity index estimation obtained with remote LIBS measurement and the transfer method versus the basicity index estimated from nominal concentrations as measured by XRF.
plotted in Fig. 4 versus the nominal values obtained by XRF at room temperature. As illustrated, there is an excellent correlation of 0.9875 between measurements with remote LIBS and those by XRF. The accuracy of the method, represented by the slope of the correlation line, is remarkable with a 1.017 which is significantly close to unit. The same plot for the Mg/Ca ratio yielded a correlation of 0.9351 and a slope of 0.9939.

4.3. High-temperature determination of in-process parameters

As an example of its versatility, the method has been applied to the determination at high temperature of the basicity index in steel slags. Basicity index, B.I., is a key parameter in the steelmaking process and is a measure of the desulphurising and dephosphorising power of the slag. Its estimation conventionally involves the measurement of Ca, Mg and Si oxide concentrations in the slag [13]:

\[
\text{B.I.} = \frac{\%\text{(CaO)} + \%\text{(MgO)}}{\%\text{(SiO}_2)}
\]

(2)

As calibration curves in previous section were obtained using Ca as an internal standard, it’s possible to isolate all the necessary information using only two calibration curves. Thus, Eq. (2) can be rewritten as a function of SiO\(_2\)/CaO and MgO/CaO concentration ratios:

\[
\text{B.I.} = \frac{1 + \frac{\%\text{(MgO)}}{\%\text{(CaO)}}}{\frac{\%\text{(SiO}_2)}{\%\text{(CaO)}}}
\]

(3)

Using Eq. (3), the basicity index was estimated using the measurements at high temperature with remote LIBS and those nominal values with XRF. Fig. 5 shows the correlation of the basicity index as estimated with the transfer method versus the XRF-based nominal values. As shown, results are in good agreement, with a slope of 1.0126 which is close to unit and an acceptable correlation coefficient of 0.9831. This result further demonstrates the suitability of the method for stand-off measurements at high temperatures.

5. Conclusions

Remote LIBS has been proven to be a suitable tool to perform measurements during the steel production process in samples at high temperature. The high temperature of in-process samples brings up several problems to conventional techniques to perform analytical measurements in the field and in real time. These problems have been overcome by the development of an analytical method involving remote LIBS along with a mathematical model which allows measurements of the concentration of samples at high temperature using a calibration curve performed with standards at room temperature. This method avoids the need to perform a calibration procedure at high temperature and is based on the development of a transfer function capable to transfer the results of measurements performed in hot samples to equivalent data useable with a room temperature calibration curve. The transfer method was also used to estimate the basicity index of the steelmaking slag samples at high temperature.

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References


