An instrument capable of reducing the quality assessment time in stainless steel-factories by a factor of 25 was built and evaluated. The instrument performs quantitative analysis based on laser-induced breakdown spectrometry (LIBS) to check for the occurrence of accidental mixing during steel production which may lead to incorrect shipping of the final products (“mix-up”). A number of developments, findings and achievements underlying the instrument itself allowed many of the variables traditionally associated with LIBS to be fixed. A laser-to-fiber robust interface was developed, which permitted safe and reliable transmission of the laser beam without gradual degradation of the fiber optic. As an additional benefit, the laser beam at the output of the fiber optics presented a homogeneous transverse profile, which allowed very flat craters to be produced. A depth profile study of stainless-steel components was used to obtain reproducible analytical results on stainless-steel samples with different surface finishes. Enhanced off-axis light collection resulted in better signal-to-background ratios without significant signal drift. Multivariate calibration for elemental analysis with LIBS proved to be a valuable tool for the correction of matrix effects and spectral interferences in certain cases. The assessment of “mix-up” was accomplished with a success rate of 100% in all the tests carried out with real samples.

Introduction

Laser-induced breakdown spectrometry (LIBS) is a well known technique owing to its ability to yield time- and space-resolved analytical results from a wide variety of samples, with little preparation and sampling rates as low as several nanograms. With detection limits typically in the ppm range, the main drawbacks frequently attributed to LIBS are high background spectra—at atmospheric pressure, relatively high RSDs and matrix effects which, up to now, have prevented a multipurpose implementation of the technique. However, developments in laser sources have contributed to more reproducible plasma generation, and the introduction of intensified solid-state detectors has made it possible to overcome some of these drawbacks by delaying and gating the multichannel detector readout. Other approaches to the variables involved in LIBS have been reported in a number of studies pioneered by Brench and Cross, concerning the fundamentals of the interaction between lasers and matter, the surrounding atmosphere, sample properties and sample temperature, among others. A significant share of the research effort has been devoted to elemental detection and determination in a wide variety of matrices. Finally, other studies have reported numerous applications, many of them claiming the possibility of further integration in industry. Gornushkin et al. have recently reported a method which introduces rank correlation for the identification of samples belonging to a series of cast iron standards of similar composition. Although the system is able to provide instant classification, it requires user intervention for sample handling. To the authors’ knowledge, only one paper reporting an automatic inspection system has been published so far. Noll et al. developed a system which identifies steel grades of elbow-like parts and marks them accordingly. The identification is based on a classical two-dimensional cluster pattern recognition algorithm using emission line intensity ratios.

Despite its effectiveness, the method is unable to provide even an approximate composition of the part, an aspect which is frequently required by customers. In fact, stainless-steel manufacturers must provide customers with a quality certificate stating the chemical composition and a reference code in connection with the so-called heat number, among others. The heat is the procedure in which the molten content of the converter is dumped in various slabs and left to solidify. Identification errors inducing a “swap”—or “mix-up”—of the final products may occur during processes further to the heat, such as cold or hot rolling. In order to overcome such problems a sample is cut from the final rolled product at the delivery time and sent to the laboratory where it is prepared for X-ray fluorescence analysis and then compared with the composition of the corresponding heat probe. This is a time-consuming procedure lasting no less than 15 min per sample, which is very expensive in terms of productivity.

In this work, the development of a faster LIBS-based alternative is presented. The authors describe the design and analytical figures of merit (AFOM) of a fully automated prototype capable of analyzing a reduced set of steel components in less than 36 s without prior sample preparation. The instrument, integrating a robotic arm for sample handling, compares the composition of the finished samples with that of their corresponding heat samples and checks for the occurrence of possible “mix-up” between consecutive series. Seeking robustness, the laser and the plasma emissions are guided via fiber optics, making use of specifically developed optical arrangements. Finally, a software program has been written which includes all functions needed for detection of sample presence, robot commanding, laser firing, data acquisition and processing, as well as for performing self-calibration of the instrument using a collection of certified reference materials.

Instrumental

A schematic representation of the instrument set-up is presented in Fig. 1. As shown, the main components are a

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LIBS system, an industrial robot and a PC. The LIBS system used a Q-switched Nd:YAG laser source (Model Ultra CFR from Big Sky Laser, Bozeman, MT, USA) operating at 1064 nm. The spectrograph was a crossed Czerny–Turner (F/3.7, focal length = 125 mm, entrance slit = 50 µm, grating 3600 grooves mm⁻¹) from Oriel (Stratford, CT, USA). It was equipped with an Instaspec IS401 CCD detector [front illuminated, UV-coated, 1024 (h) × 128 (v) elements] from Andor Technology (Belfast, UK), operated in full vertical binning readout mode. Interfacing between the computer and the robot was carried out through the auxiliary I/O of the Andor CC101 CCD controller card by conditioning the electrical signals. Overall set-up and commanding of the laser was done via the RS-232 port of the PC. The TTL signal of the Q-switch was used as a trigger for the CCD. This scheme introduces a fixed delay of 0.5 µs between the laser pulse and the beginning of the acquisition cycle, which is of the order of that needed to reduce the presence of very intense backgrounds.

Two interfaces were developed corresponding to the laser–fiber incoupling and to the sample holder. The former, outlined in Fig. 2, consists of a three-axes adjustable flange containing the focusing lens (BK7, diameter = 6 mm, plano-convex, f = 15 mm) and the fiber connector (ferrule, diameter = 1.1 mm). The fiber used to transport the laser light was made of fused silica with a 540 : 600 µm core-to-cladding ratio and 2 m length. The design of the interface covered, among others, two critical aspects in order to couple the maximum laser energy to the fiber optic without damage: (i) tight fiber tip positioning beyond the focused neck of the laser in order to avoid the high-irradiance spot falling inside the fiber, (ii) use of a bare fiber tip standing 15 mm out of the copper connector. Current incoupling has been running for 1.8 × 10⁶ laser shots with no degradation of performance. All fiber arrangements were designed and prepared at the laboratory, polishing their ends to a 0.3 µm grain size.²⁴–²⁵

A dual optic guide configuration was adopted with the aim of simplicity. The focusing arrangement is shown in Fig. 3. It consists of two plano-convex lenses which, from fiber to sample direction, work by first collimating (L1: fused silica, diameter = 25 mm, f = 50 mm) and then focusing (L2: fused silica, diameter = 25 mm, f = 30 mm) the laser light with a magnification factor of 0.6. The resulting focused spots are theoretically 325 µm in diameter which corresponds to crater diameters of about 500 µm after 150 laser shots. Plasma emission was collected at an angle of 55° to the laser using a fiber optic with the same characteristics as that used to guide the laser. A specific connector was made containing both the fiber end and a plano-convex lens (fused silica, diameter = 7 mm, f = 10 mm) to improve light throughput. The end of the fiber was attached to the spectrograph using two plano-convex lenses (fused silica, diameter = 10 mm) matching the numerical apertures of both the fiber and the spectrograph.

**Fig. 1** Schematic diagram of the instrument: (1) laser power supply; (2) laser head; (3) laser–fiber incoupling module; (4) fiber optics; (5) sample chamber; (6) sample; (7) robot; (8) robot power supply; (9) spectrograph; (10) CCD; (11) PC; (12) power supply and data connections.

**Fig. 2** Laser–fiber incoupling module: (1) laser head; (2) X–Y adjustable flange; (3) micrometric adjustment; (4) lens; (5) fiber optic; (6) fiber connector; (7) fixing screws.

**Fig. 3** Sample chamber: (1) fiber optics; (2) laser focusing arrangement; (3) sample; (4) plasma; (5) sample receptacle; (6) light collection; (7) connector fixing screw; (L1) collimating lens; (L2) focusing lens; (L3) light collection lens.

**Results and discussion**

**Sample holder and detection of new sample**

The instrument was designed to receive the samples in a tray attached to the robot arm. Two main problems were identified both associated with the wide diversity of sample sources and morphologies: (i) simplicity of handling with the robot and (ii) tight adjusting of the laser focus which is of great importance to the reproducibility of the analysis. As shown in Fig. 1, the first problem was overcome with a design consisting of a tray made of stainless-steel which was attached to the robot arm. Details of this tray are outlined in Fig. 3. The tray and the optics were mounted together with a holder (not shown in Fig. 3 for ease of viewing). An orifice of 2 cm in diameter provided optical access to the sample from its bottom. As the distances between the sample and optics were held constant, this configuration was able to deal with samples of different thicknesses without further adjustment of the focusing and collection optics. Detection of a new sample was carried out by monitoring the Hg(I) 334.14 nm line coming from the room illumination which was interrupted on sample arrival. The signal depletion was detected and used for triggering the analysis.

**Samples**

Stainless-steel samples of different grades were provided by ACERINOX (Los Barrios, Cádiz, Spain). The composition of all the samples is detailed in Table 1.

**Table 1** Composition of stainless-steel samples

<table>
<thead>
<tr>
<th>Grade</th>
<th>Composition (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>316</td>
<td>C: 0.04, Si: 0.02, Mn: 2.1, P: 0.015, S: 0.01, Cr: 16.9, Ni: 11.8</td>
</tr>
<tr>
<td>304</td>
<td>C: 0.04, Si: 0.02, Mn: 5.5, P: 0.015, S: 0.01, Cr: 17.5, Ni: 8.6</td>
</tr>
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</table>

"‡"...
Preparation of sample surface

The poor precision yielded by LIBS measurements on a fresh sample surface is well known. Such behavior is commonly attributed to the topography of the sample surface and to surface contamination. Although at high laser irradiances ($>28\ \text{GW cm}^{-2}$) the influence of surface roughness on precision is negligible, in the present work the samples were irradiated at $5.7\ \text{GW cm}^{-2}$ due both to limitations imposed by the fiber optics and to reflection losses. On the other hand, heat samples present considerable surface oxidation. A depth profile of iron is shown in Fig. 4 which is representative of other elements in the matrix. According to the plot, about 150 shots are necessary to achieve a stable signal level. The three bottom plots correspond to the signal RSD calculated from sets of 50, 100 and 200 consecutive points along the profile corresponding to short-, medium- and long-term signal behavior, respectively. In all samples examined, the accumulation of 100 data points was found to be adequate to improve signal precision. Microscope examination of craters obtained after 150 laser shots revealed complete removal of the oxide layer for heat samples and significant modification of the original surface for finished samples with flat-bottomed craters regardless of the original sample roughness, as illustrated in Fig. 5. A spectrum obtained by accumulating 100 laser shots after a previous surface treatment with 150 shots is shown in Fig. 6. The spectrograph was centered at 342 nm, seeking the maximum number of elements to be simultaneously measured with minimum spectral interferences. In spite of this, few emission lines were free from major spectral interferences owing to the complexity of the stainless-steel matrix. Attempts were made to improve the SBR by spatially resolving the plasma emission, although better values of the SBR of 10 for the Cr(II) 336.805 nm line were found, the degradation of signal precision (RSD) was remarkable versus the integration of the whole emission.

Collection at $55^\circ$ to the laser was preferred to on-axis or $90^\circ$ collection schemes as it showed the best compromise between SBR and RSD.

Although the maximum repetition rate allowed by the laser

---

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>Mo</th>
<th>Ti</th>
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<td>16.27</td>
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<td>0.02</td>
<td>0.01</td>
<td>—</td>
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<td>B</td>
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<td>16.17</td>
<td>0.13</td>
<td>0.08</td>
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<td>—</td>
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<tr>
<td>C</td>
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<td>18.39</td>
<td>8.08</td>
<td>0.30</td>
<td>0.34</td>
<td>0.004</td>
<td>1.76</td>
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<tr>
<td>D</td>
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<td>18.19</td>
<td>8.22</td>
<td>0.32</td>
<td>0.29</td>
<td>0.004</td>
<td>1.88</td>
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<td>1.155</td>
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<td>0.029</td>
<td>1.418</td>
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<td>F</td>
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<td>0.019</td>
<td>0.642</td>
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<td>G</td>
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<td>11.41</td>
<td>8.082</td>
<td>0.113</td>
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<td>65.737</td>
<td>16.134</td>
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<td>2.008</td>
<td>0.021</td>
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<td>13.794</td>
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<tr>
<td>I</td>
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<td>17.025</td>
<td>2.613</td>
<td>1.954</td>
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<td>J</td>
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<tr>
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<td>12.433</td>
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<td>28.34</td>
<td>39.745</td>
<td>1.542</td>
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<td>0.007</td>
<td>0.743</td>
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<td>80.54</td>
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<td>0.01</td>
<td>0.099</td>
<td>0.18</td>
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<tr>
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<td>16.95</td>
<td>11.11</td>
<td>0.39</td>
<td>2.11</td>
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<td>1.38</td>
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<td>V</td>
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<td>11.22</td>
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<td>0.06</td>
<td>0.04</td>
<td>0.18</td>
<td>0.28</td>
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<tr>
<td>Y</td>
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<td>17.24</td>
<td>10.77</td>
<td>0.39</td>
<td>2.1</td>
<td>0.037</td>
<td>1.27</td>
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</table>

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Fig. 4 Depth profile of iron (□) for a stainless-steel sample. The Fe(I) 358.119 nm line intensity is plotted versus the laser shot number (left axis). In the right axis, each point of the plots represents the RSD value calculated for 50 (●), 100 (○) and 200 (△) consecutive intensity values of the depth profile.

Fig. 5 Scanning electron micrograph of a crater in a stainless-steel sample obtained after 150 laser shots at a 20 Hz repetition rate and a 5.7 GW cm$^{-2}$ irradiance. Crater diameter measures 500 μm. Magnification factor, ×120.
was 20 Hz, its performance decrease under this regime induced an increase of the signal RSD to the 8–11 % level. For this reason, as a compromise between speed of analysis and precision, the repetition rate was maintained at 20 Hz for the 150 shots needed for sample preparation, and then decreased to 5 Hz during the 100 shot signal acquisition. This practice yielded a sample analysis time of less than 28 s and RSD values better than 2%. The processing time lasted about 1 s in a 300 MHz PC.

Data processing and quantitative analysis

As with other atomic emission spectrometric methods, the influence of matrix components on LIBS poses a major problem for the quantification of complex matrices. Fig. 7(a) illustrates an example where the iron concentration is plotted versus the intensity of the Fe(I) 358.119 nm line for several stainless-steel samples. Although first- and second-order polynomial fittings often yield good results for calibration graphs with binary samples, there is no apparent correlation between iron concentration and intensity, as shown in Fig. 7(a). This indicates that further variables are involved when more than two components are present resulting in intensity changes of the emission lines. Such changes are due to the physical and chemical nature of the elements integrating the matrix, which influences the evaporation rates and other processes occurring in the plasma. Also, spectral interferences may induce changes in line intensities. Consequently, alterations in the measured line intensities are systematic and can be corrected.27 Accordingly, the intensity $I_j$ of an emission line $j$ for an element $i$ could be expressed as a function of the concentration $C_i$ of the $n$ elements present:

$$I_j = I(C_1, C_2, C_3, \ldots C_n)$$  (1)

Thus, expressing the concentration of a component as a function of the intensity of emission of one line of every element,

$$C_i = C(I_1, I_2, I_3, \ldots I_n)$$  (2)

makes it possible to perform a calibration for element $i$ via a multivariate analysis with $n$ independent variables. In its simplest form, eqn.(2) can be written as a linear combination of the intensities multiplied by their respective slopes, $s_i$, plus an intercept, $b_i$:

$$C_i = b_i + \sum_{j=1}^{n} s_i I_j$$  (3)

A multivariate linear analysis was performed with the data in Fig. 7(a) using the emission lines coded as I, J, G, A, C and E. Such a statistical tool made possible the selection of the emission lines having a significant contribution.28–30 When the observed $t$-value for a given variable is higher than the tabulated critical $t$-value, it can be concluded that the particular variable is not playing a significant role in the regression model. The observed $t$-value for each variable is obtained from the ratio of the estimated slope of the calibration graph to its corresponding standard error. According to the former criterion, lines A, C and E were discarded as they did not contribute significantly to the regression model, which finally yielded a correlation coefficient $R^2 = 0.9891$. Hence, the equation for the determination of the iron concentration could be written as follows:

$$C_{Fe} = B_{Fe} + s_{Ni}I_{Ni} + s_{Cr}I_{Cr} + s_{Fe}I_{Fe}$$  (4)

Such an expression describes the linear dependence of the estimated iron concentration, $C_{Fe}$, on the intensity of emission...
The main objective of this work was the construction and evaluation of an instrument capable of reducing the time needed to perform the assessment of "mix-up" in stainless-steel factories. This objective has been accomplished via a number of developments, findings and achievements underlying the instrument itself which have allowed many of the variables traditionally associated with LIBS to be kept under control. The assessment of "mix-up" was accomplished with a success...
rate of 100% in all the tests carried out with real samples. However, manganese had to be discarded as the precision yielded by the instrument for this element could not meet the strict requirements of the quality assessment. It must be noted that because of the lack of automation and poor resolution of the spectrograph available for this study, the number of accessible emission lines was significantly reduced. In order to deal with analytical problems in a complex matrix such as steel, the spectrometer should be modified to cover a much wider spectral range without a lack of spectral resolution. The overall time of analysis with the present instrument reduces the average time currently spent in the factory by a factor of 25, which may certainly be unnecessary, but provides an idea of the potential of the LIBS technique implemented with a fully automated instrument for industrial survey purposes.

Although the system has been applied to stainless-steel analysis the instrument can be used for the analysis of many types of materials, offering a wide range of potential applications such as in mining extraction or classification of solid wastes for recycling.

Acknowledgements

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