Open-path laser-induced plasma spectrometry for remote analytical measurements on solid surfaces

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Abstract

Open-path laser-induced plasma spectrometry has been studied for elemental analysis at a distance of 45 m from the target. The 230-mJ pulsed radiation of a Q-switched Nd:YAG laser at 1064 nm has been used to produce a plasma on the sample and light emission has been collected under an off-axis open-path scheme. Under such conditions, the main variables influencing the signal response such as beam focal conditions, laser incidence angle and laser penetration depth have been identified and diagnosed on the basis of spectral signal-to-noise ratio considerations. The incidence angle is critical beyond 60°. Crater morphology and ablation rates have been studied also. A semi-quantitative analysis of several stainless steel grades has been implemented using a pattern recognition algorithm, which allowed to discriminate successfully the samples on the basis of their variable content in alloying elements. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Optical remote sensing techniques provide the capability to remotely monitor and measure trace gases and aerosols by guiding a laser beam either across a large open atmospheric path (direct sensing) or through fiber optics (indirect sensing) towards the sample of interest [1–4]. Although the fiber approach indeed makes possible the analysis at remote places which are unreachable by other means, indirect sensing is of restricted application in those cases where aggressive chemical or temperature environments may affect the condition of the probe, or when large areas must be analyzed. In such cases, the open path approach is more suitable as it is demonstrated by a wide range of applications covering environment monitoring in atmospheric [5,6], ocean [7,8] and ground media [9,10], large-field area mapping [11,12], agricultural purposes [13,14], and cultural-heritage conservation [15,16], among many others. This wide applicability is feasible due to the fact that the
Fig. 1. Schematic setup. (1) Nd:YAG laser; (2) planoconcave lens; (3) planoconvex lens; (4) achromatic refractor telescope; (5) spectrograph; (6) CCD detector; (7) PC computer; (8) data and control.

Fig. 2. OP-LIPS spectra of an AISI 304 stainless steel sample obtained at a 40-m distance by accumulating 100 laser shots over the same position. Laser pulse energy was 230 mJ.
information is gained from the light recovered by a receptor, which commonly measures absorption or scattering of the probe beam, or fluorescence or Raman radiation emitted by the analyte. An extensive review on laser remote sensing techniques has been recently published by Panne [17]. Although atomic emission spectrometry has been studied for fiber supported applications [18–20], so far the technique has not been explored systematically for open-path remote sensing. It is clear that the lack of practical excitation sources capable to work remotely from the spectrometer is the main reason. In a previous work [21], the authors presented a prospective study intended to minimize or eliminate the risky and lengthy hot-sampling operations during the steel-making process using laser-induced plasma spectrometry (LIPS). The feasibility of LIPS for samples heated in a laboratory muffle up to 1200 °C was demonstrated with a system separated 0.5 m from the sample. The effects of sample temperature on iron, chromium, nickel and manganese LIPS signals revealed up to sixfold improvements for temperatures in the range 25–1100 °C.

Recently, Cremers et al. [22] presented the application of LIPS to the stand-off analysis of soils up to a distance of 19 m for space exploration. Special attention was paid to investigate the suitability of the technique for the analysis of soils in a CO₂ atmosphere similar to that in Mars which additionally provides analytical improvements owing to the reduced-pressure in the chamber used to perform the simulation.

In the present work, open-path laser-induced plasma spectrometry (OP-LIPS) has been investigated for remote elemental analysis of solids placed up to several tens meters from the spectrometer. We outline the feasibility of this approach and take a first step toward the investigation of its potential. The pulsed radiation of a Q-switched
Nd:YAG laser at 1064 nm has been used to induce a plasma on the sample and the emission has been collected under an open path scheme up to a 45-m distance. Under such conditions, the main variables affecting the signal response such as beam focal conditions, laser incidence angle, laser penetration depth, light collection efficiency, have been identified and diagnosed on the basis of spectral signal-to-noise ratio considerations. Crater morphology and ablation rates have been studied also. The system performance for both identification purposes and for semi-quantitative analysis is discussed.

2. Experimental setup

A schematic diagram of the instrument setup is shown in Fig. 1. The main components of a LIPS system are shown with the only exceptions of the sample holder and the necessary modifications made to the focusing and collection elements. A Q-switched Nd:YAG laser (Continuum, Surelite Y-20) was used to produce 230 mJ, 5 ns pulses at 1064 nm. A Galilean telescope was built to focus the laser beam to the far field. Hence, the 6 mm Gaussian beam was directed firstly to a planoconcave lens (BK7, \(d = 25.4 \text{ mm}, f = -25 \text{ mm}\)) and then focused to the sample surface with a planoconvex lens (BK7, \(d = 76.2 \text{ mm}, f = 300 \text{ mm}\)). By raising the spacing between both lenses — which amounts to 273 mm for a 12\(\times\) collimated output — the focus is brought from infinite to the actual working distance. Such magnification in conjunction with the energy distribution of the beam reaching the sample ensured the absence of undesired air breakdown while the working distance between instrument and sample was modified by adjusting the spacing between both lenses with a micrometric linear positioner. Light emitted by the plasma was collected with a conventional achromatic refractor telescope (\(d = 60 \text{ mm}, f = 400 \text{ mm}, f/8.3\)) in an off-axis configuration to the laser. This scheme provided a more transparent light-collection path where dust particles in the laser path were ionized. The telescope eye-piece flange was adapted to the entrance slit of a 0.5-m, \(f/8\) Czerny–Turner spectrograph equipped with a triple

<table>
<thead>
<tr>
<th>AISI steel grade</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Ti</th>
<th>Nb</th>
<th>Mn</th>
</tr>
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<tr>
<td>303</td>
<td>18.19</td>
<td>8.22</td>
<td>0.29</td>
<td>–</td>
<td>–</td>
<td>1.88</td>
</tr>
<tr>
<td>304</td>
<td>18.13</td>
<td>10.13</td>
<td>0.08</td>
<td>–</td>
<td>–</td>
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<tr>
<td>316</td>
<td>17.24</td>
<td>10.77</td>
<td>2.10</td>
<td>0.037</td>
<td>0.045</td>
<td>1.27</td>
</tr>
<tr>
<td>316Ti</td>
<td>16.95</td>
<td>11.11</td>
<td>2.11</td>
<td>0.247</td>
<td>0.040</td>
<td>1.38</td>
</tr>
<tr>
<td>430</td>
<td>16.17</td>
<td>0.13</td>
<td>0.02</td>
<td>–</td>
<td>–</td>
<td>0.29</td>
</tr>
<tr>
<td>430Nb</td>
<td>17.86</td>
<td>0.20</td>
<td>0.04</td>
<td>0.280</td>
<td>0.527</td>
<td>0.28</td>
</tr>
</tbody>
</table>
Fig. 5. Signal sensitivity to sample topography at WD = 40 m. Left: signal-to-noise ratio (SNR) for the 540.97 Cr(I) emission and the normalized signal are represented together vs. the laser angle of incidence (see text for details on signal normalization). Right: photographs of the corresponding spots in the steel sample.

grating turret (300, 1200 and 2400 l mm\(^{-1}\); Chromex, 500-IS, reciprocal linear dispersion is 1.6 nm mm\(^{-1}\)). At the spectrograph exit flange, an iCCD camera (768\(\times\)512 pixel; Stanford Computer Optics, 4Quik05) was used to detect the dispersed light. In order to synchronize the acquisition to the laser event, a TTL signal from the Q-switch electronics was guided to the CCD camera whose internal electronics allowed to generate a delay of 4\(\times\)10\(^{-7}\) s and to drive the intensifier gate of 1.2\(\times\)10\(^{-6}\) s. The given timing values were optimized to attain the higher signal to background ratio possible for the 540.97 nm Cr(I) emission line. Images acquired by the camera were captured with a frame grabber card (Data Translation, DT55) and then processed (Stanford Computer Optics, 4Spec software) with a PC computer to produce background-subtracted spectra. Only the 20 illuminated CCD rows were captured and processed to improve both signal-to-noise ratio (SNR) and acquisition time. Even though, a maximum acquisition rate of four spectra per second could be achieved due to the low bandwidth of the ISA bus between the frame grabber and the PC.

2.1. Samples

ACERINOX, S.A. (Los Barrios, Cádiz, Spain) provided stainless steel samples of different grades whose composition is detailed in Table 1. All analyses in the present study have been done at room temperature in order to both simplify sample handling and to work under a worst-case scenario exempt from the benefit of improved signal emission occurring for samples at high temperature.

3. Results and discussion

3.1. OP-LIPS spectra

Previous to elemental analysis based on OP-LIPS, the signal response was evaluated in terms of dependence with sample topography and with beam focal conditions for a given laser and collec-
Fig. 6. OP-LIPS spectra obtained at WD = 45 m comparing the emission of six different stainless-steel grades to that of pure Nb, Ti, Mo and Ni. Vertical dotted lines indicate differencing spectral features. Fifty laser shots over the same sample position were accumulated to register each spectrum. Scaling has been altered for ease of viewing.

3.2. Sensitivity to focal conditions

The response of the 540.97 Cr(I) emission intensity to changes in sample position is presented in Fig. 4. The working distance (WD, the distance from the focusing lens to the sample) was changed from 35 to 45 m while keeping the laser focusing conditions unchanged. For the sake of clarity, the distance from sample to the laser focus (DTF) has been plotted on the abscissa axis rather than WD, with negative values of DTF corresponding to larger WD setting. As shown, a maximum SNR of approximately 78 was found at DTF = 0 m. From that point, the SNR follows a nearly Gaussian behavior as the absolute value of DTF increases, showing a somewhat asymmetrical bell shape. This effect was attributed to both thermal effects and aberrations induced by the simple focusing optics employed.
Fig. 7. Three-dimension space showing how projections of the nickel, molybdenum and titanium raw signals corresponding to several stainless steel samples, cluster to produce the discriminating pattern indicated by the dotted lines. AISI steel grades are: ■, 304; ●, 303; ▲, 316; ●, 316Ti; ★, 430; ✶, 430Nb.

which both optical axes, the one of the collection unit and the one of the laser focusing unit, intercept right at their focal points, resulting in an asymmetrical collection efficiency at either side of the focus. The inset in Fig. 4 shows a photograph series which is representative of the effect of beam focal conditions on crater morphology. A progressive increase of the overall spot dimensions, along with a vanishing of the central spot is observed with the increasing absolute values of DTF. Enhanced information was obtained by digitally processing the images (in lighter gray). This operation revealed a certain degree of homogenization of the laser energy distribution throughout the irradiated sample area for larger absolute values of DTF, which is a remarkable detail from the analytical point of view. Bulk representivity of the measurement improves as larger sample areas are interrogated with a more homogeneous beam probe, resembling a more adequate approach for a remote analysis configuration. The signal precision calculated for the central ±1 m DTF range yielded a 14% R.S.D. which can be considered as outstanding taking into account the decisive role that focal conditions usually play in laboratory-scale LIPS measurements. Despite the high tolerance to sample positioning, it is worth mentioning that the adjustment of the focusing conditions to a given WD resembles the same difficulty as for a lab scale experiment. Moreover, the signal is strongly dependent on sample position for DTF values out of the mentioned range. In order to compensate for this issue, the Cr signal was normalized to the 537.14 Fe(I) emission intensity. The results are plotted in the upper trace of Fig. 4. As shown, a steady behavior of the normalized signal was observed along the whole 10 m DTF range. The precision is 9.1% R.S.D. for such interval and improves to 6.3% for the central 8-m DTF range, demonstrating the system capability to produce analytically treatable signals even at extremely defocused conditions (DTF= ±5 m). Moreover, when the instrument was focused to WD=45 m and DTF was set to 0 m, the SNR was restored to approximately 71, corresponding to a sensitivity loss of only a 9% in SNR and a 15.7% in raw
signal terms for a WD increase of 5 m over 40 m — which is approximately 12.5%. This result suggests that open-path analysis maybe feasible without instrument modifications at least at a small WD range beyond 45 m.

Under these conditions, 6750 laser shots were fired over the same position of an iron reference sample. An average ablation rate (AAR) of 1.2 nm per pulse was calculated from the depth of the resulting crater. Plasma emission was registered during the whole experiment and a depth profile for the 537.14 Fe(I) emission line was plotted. A 17% R.S.D. was found, which could be partly attributed to the 6.3% signal drift shown by the iron signal.

3.3. Sample topography

Owing to the nature of the technique, a common situation in OP-LIPS is devised in which either the sample is not at a right angle to the laser beam, or even the bulk being under such configuration, the actual point of the surface irradiated by the laser may not be at a normal incidence. This fact can greatly influence the results of analytical measurements. Consequently, the sensitivity to sample orientation was studied by plotting the SNR of the 540.97 Cr(I) emission versus the laser incidence angle as shown in Fig. 5. As shown, the SNR follows a small decay trend for increasing incidence angles, presenting an abrupt fall for angles over 40°. Photographs of the ablated spots are shown in Fig. 5, top. The central crater in the spot — where the plasma expands from — stretches progressively as the angle is raised up to 50°. For such an angle, where the calculated fluence has decreased by 23.4% over that at normal incidence, the central crater almost fades inside the larger spot. This fact along with the higher reflectivity typical from such incidence angles explains the stepped signal decrease beyond 40°. Under the given conditions, any analysis performed beyond such an incidence angle would render biased results if no correction was applied. For this purpose, the Cr signal was normalized as above. The resulting trace, also plotted in Fig. 5, remains nearly constant (R.S.D. = 1.7%) for angles up to approximately 50° and slightly falls at 60°.

Although the signal is efficiently corrected for a wider angle range, the drastic SNR reduction at 60° suggest no further possibility of improvement than raising the fluence which reaches the sample.

3.4. Sorting of steel grades

Fig. 6 shows ten OP-LIPS spectra obtained at 45 m accumulating 50 laser shots over the same sample position. As illustrated, spectra corresponding to six different stainless-steel grades are compared to niobium, titanium, molybdenum and nickel reference spectra, indicating several emission lines, which allow to identify the six steel grades. This possibility has been used for the design of a pattern-recognition algorithm based on a three-dimensional space in which nickel, molybdenum and titanium signals are in the axes. To demonstrate the strength of the method, only the raw emission signals after accumulating 50 laser shots have been used without further normalization. The example in Fig. 7 shows that, despite the low precision, signals corresponding to similar sample concentrations cluster together to produce well defined groups which enable to successfully classify samples of the six steel grades.

4. Conclusions

OP-LIPS has been demonstrated as a technique capable to perform remote analysis in the complex stainless steel matrix. The low influence of focusing conditions on the normalized analytical signal seems to grant a great versatility for the analysis of irregularly shaped samples. On the other side, a certain dependence on laser incidence angle has been found which may influence the analysis results for laser incidence angles in excess of 60°. Even though, benefits drawn from remote operation with OP-LIPS — ensuring not only speed and simplicity of analysis, but also safety of both personnel and equipment — by far counterbalance the mentioned difficulty. Despite the system has been applied to stainless steel analysis, its applicability goes far beyond the industrial quality control purposes. A wide range of niche applications such as analysis in inaccessible or harmful
areas, environmental monitoring or conservation of cultural heritage, are currently under study.

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