Remote laser-induced plasma spectrometry for elemental analysis of samples of environmental interest

C. López-Moreno, S. Palanco and J. J. Laserna*

Department of Analytical Chemistry, Faculty of Sciences, University of Málaga, E-29071 Málaga, Spain. E-mail: laserna@uma.es

Received 8th June 2004, Accepted 31st August 2004
First published as an Advance Article on the web 23rd September 2004

Remote laser-induced plasma spectrometry has been demonstrated as a valuable analytical tool both for qualitative inspection and quantitative determinations on environmental samples. For this objective, the pulsed radiation of a Q-switched Nd:YAG laser at 1064 nm has been used to produce a plasma in a remote sample, the light emission being collected under a coaxial open-path optical scheme and guided towards a spectrograph and then detected by an intensified CCD. A prospective study has been carried out to assess the suitability of the technique for the remote analysis of samples from a coastal scenario subjected to a high industrial activity. All the measurements have been done in the laboratory. Among the main factors influencing the analytical results, sample moisture and salinity, sample orientation and surface heterogeneity have been identified. The presence and distribution of Fe and Cr as a contaminant on sample surface has been quantified and discussed for samples including soil, rocks, and vegetation. At a stand-off distance of 12 m from the spectrometer to the sample, limits of detection in the order of 0.2% have been obtained for both elements.

Introduction

Industrial environments are subjected to a highly acoustic, visual and chemical contamination. Continual monitoring of the effects of industrial activity, whether in ground, air or aqueous media is often necessary to keep industrial impact to acceptable levels. The inaccessibility of some locations and their hostile environments are challenges for the development of analytical techniques capable to afford the difficulties of such analytical problems.1 Real-time, non-preparative, in situ or remote-capable are among the desirable features from candidate elemental characterisation techniques.

It has been more than 40 years since it was first noticed that plasma emission of a high-power pulsed laser irradiating a material contains sufficient spectroscopic information for the elemental analysis of that material. In the intervening period there have been numerous investigations, application demonstrations, and instrument variations reported by researchers, technologists, and world-wide instrument manufacturers using the technique that has become known as laser-induced breakdown spectroscopy (LIBS) or laser-induced plasma spectroscopy (LIPS).2–5 LIPS is an elemental analysis technique that is an alternative to established analysis methods such as X-ray fluorescence, atomic absorption and emission spectroscopy, mass spectrometry and neutron activation analysis. In the present state of development, only under ideal circumstances LIPS can compete with these technologies in terms of analytical figures of merit, that is, limits of detection, precision, accuracy and so forth. However a number of appealing characteristics make LIPS of interest for analytical purposes including fast, real-time analysis, in situ field operation and analysis without sample preparation.6–10 One of the unique capabilities of LIPS is to remotely monitor the elemental composition of solids. Remote LIPS analysis can be implemented using optical fibers for transmitting the light to or from the sample.11,12 However, it is often more interesting to use an open path approach in which the interrogating laser beam and the returning light are transmitted through the atmosphere. With this configuration, remote, difficult-to-access locations and hostile environments can be analyzed without the physical presence of the operator.13–19 In previous works, the capabilities of remote LIPS have been explored by our group. The technology has been tested and evaluated under laboratory and field conditions for analytical identification of steel grades at 45 m from the instrument14 and for real-time analysis of hot solid steel and liquid steel at about 1420 °C.15 For this purpose several instruments have been developed which incorporate the latest advances in ns laser sources and parallel detection systems, and newly developed concepts for laser beam delivery and optical collection of the returned light.

In the present work, remote LIPS is demonstrated as a valuable analytical tool for both qualitative inspection and quantitative determinations on environmental samples proceeding from a coastal scenario subjected to high industrial activity. A number of issues influencing the analytical results such as moisture, salinity, sample orientation and heterogeneity have been evidenced. LIPS capabilities for spatial analysis are exploited to study the presence, concentration and distribution of Cr as a contaminant in a widespread of samples including soil, rocks, and vegetation.

Experimental

The experimental setup is sketched in Fig. 1. The laser source is a Q-switched Nd:YAG laser providing a pulsed output of up to 1500 mJ and 12 ns in a flat profile of 12 mm in diameter. The beam guiding component is an 8.9 x beam expander integrated by a couple of 1064 nm antireflection-coated best-form BK7 lenses with effective focal lengths of −22.25 mm and 198.84 mm. Attending to geometry, a coaxial scheme in which the laser beam and the plasma emission share the same optical axis19 has been employed in the present work. A flat circular mirror 300 mm in diameter tilted 45° is used to bend the return path towards the collecting optics. A central aperture 110 mm in diameter was drilled in this mirror to allow the expanded laser beam to pass through. A commercial Newton telescope with F/4 and a primary mirror of 200 mm in diameter was employed for light collection. The plasma is imaged with a variation in its position of up to 120 mm depending upon the sample distance. Given such a large variation in plasma image position, the use of a fused-silica fiber optic cable (200 μm/250 μm core/cladding) was considered as an alternative to directly
coupling of the light to the spectrograph \( (f = 27.5 \text{ cm}, 600 \text{ l m}^{-1} \text{grating}) \). Although this approach presents clear design, construction and adjustment advantages, it also produces light losses at the optical surfaces which must be inserted between the telescope and the entrance slit of the spectrograph. A 200-\( \mu \text{m} \)-core fiber optic cable would deliver no more than a \((0.96)^2\) throughput owing to losses in surface reflections. Imaging the fiber end to the slit would produce a spot of 200 \( \mu \text{m} \times (3.8/2.27) = 340 \mu \text{m} \) in diameter (3.8 and 2.27 being the F/# of the spectrograph and the fiber optic cable, respectively). The light throughput to the spectrograph was calculated by integrating the equation of the circumference defined by the focused spot between the limits given by the slit width.\(^{19}\) Assuming a minimum 1% loss per surface using an antireflection coating at each of the two lenses required, the overall light throughput was calculated by integrating (1024 × 128 pixel intensified CCD) and a dedicated software running in a personal computer. An integration gate of 1.5 \( \mu \text{s} \) with a delay time of 0.9 \( \mu \text{s} \) referred to the laser pulse yielded the best signal to continuum ratio.

**Samples**

All samples used in this work are actual samples collected from a high industrial activity area. Petrochemical and metallurgical factories, a power station and high maritime traffic entail the possible sources of contamination of this area. Selection of the samples was done obeying to different criteria such as orientation, distance to the contamination source, matrix composition, as well as the presence of humidity or salinity. A detailed description of the samples can be found in Table 1. All experiments were run at the laboratory at a stand-off distance of 12 m from the sample.

**Results and discussion**

**Remote LIP spectra and depth-resolved analysis**

One of the main advantages of LIPS as a field-deployable technique includes the capability for fast sample identification through the in-depth analysis of its elemental components without a prior surface preparation nor having to reach the sample location. As a proof of concept, Fig. 2 illustrates the remote LIP spectra acquired at 12 m from sample KS-04. The main spectral features have been assigned in the plot. As shown, the spectrum corresponding to the sample surface reveals the presence of Cr emission, such element not being detected in the rock matrix. A similar case is Fe whose emission is clearly more intense in the surface than in the sample matrix. Fig. 2 left shows the emission depth profile of the main emission found in spectra taken from sample KS-04. To improve sampling representativity, the focusing optics were set to obtain a spot size on the surface of about 1.2 mm. Separate measurements were done to ensure that channelling of the plasma in the crater (0.5 mm in depth) had a negligible influence to the resulting emission profiles. As a further measure, the depth profile shown was averaged from ten individual profiles acquired at ten close lateral positions in the sample. Each single profile was constituted by sixty spectra.

To minimize flicker influence, the peak areas of Fe, Cr, Ca and Si were normalized to Mg peak area as an internal standard. The Mg plot has been normalized to its maximum peak area value along the crater depth, to fit the same scale as the other plots. The depth axis of the profile has been calibrated to reflect the \(~10 \mu \text{m} \) average ablation rate (AAR) measured for the contamination layers under study. Although the AAR does not keep constant with the number of laser shots deposited on a single location, its use as a reasonably good estimation for the calculation of the crater depth is widely accepted. On the right side of the figure, four spectra corresponding to laser shots number 1, 11, 21 and 51 are also shown from top to bottom. As illustrated, plots corresponding to Fe, Cr, Ca and Si exhibit a steep decreasing trend for the first 20 laser shots followed by a more moderate fall up to pulse number 51. From this point, at about \(540 \mu \text{m} \) depth, the presence of Cr was not detected and a separate measurements were done to ensure that channelling of the plasma in the crater (0.5 mm in depth) had a negligible influence to the resulting emission profiles. As a further measure, the depth profile shown was averaged from ten individual profiles acquired at ten close lateral positions in the sample. Each single profile was constituted by sixty spectra.

To minimize flicker influence, the peak areas of Fe, Cr, Ca and Si were normalized to Mg peak area as an internal standard. The Mg plot has been normalized to its maximum peak area value along the crater depth, to fit the same scale as the other plots. The depth axis of the profile has been calibrated to reflect the \(~10 \mu \text{m} \) average ablation rate (AAR) measured for the contamination layers under study. Although the AAR does not keep constant with the number of laser shots deposited on a single location, its use as a reasonably good estimation for the calculation of the crater depth is widely accepted. On the right side of the figure, four spectra corresponding to laser shots number 1, 11, 21 and 51 are also shown from top to bottom. As illustrated, plots corresponding to Fe, Cr, Ca and Si exhibit a steep decreasing trend for the first 20 laser shots followed by a more moderate fall up to pulse number 51. From this point, at about \(540 \mu \text{m} \) depth, the presence of Cr was not detected and a steady behavior was found for the remaining elements under study which is indicative that the sample matrix has been reached at such depth. The sample was then cut and a dark contamination layer could be observed on top of the white

![Figure 1 Instrument setup](image)

**Table 1** Summary of the samples used for this work detailing sample location as well as remarkable observations

<table>
<thead>
<tr>
<th>Code Sample</th>
<th>Sampled location</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>KS-01 Bark</td>
<td>Weeping willow trees close to a factory</td>
<td>White dust deposited on the surface and accumulated in the crannies</td>
</tr>
<tr>
<td>KS-02 Leave</td>
<td>Weeping willow trees close to a factory</td>
<td>White dust deposited on the surface</td>
</tr>
<tr>
<td>KS-03 Soil</td>
<td>Perimeter of a factory. Same location as KS-05 and KS-06</td>
<td>Homogeneous grey colour. Seems to have a thick dust layer</td>
</tr>
<tr>
<td>KS-04 Dock rock</td>
<td>Factory dock periodically immersed in sea water at high tide</td>
<td>Porous and irregular surface. White matrix colour, brown surface with dark-white coloured spots in every nook and cranny. Manmade stone from a retaining-wall close to the shore.</td>
</tr>
<tr>
<td>KS-05 Stone</td>
<td>In the perimeter of a factory. Same location as KS-03 and KS-06</td>
<td>Grey coloured with darker grey zones</td>
</tr>
<tr>
<td>KS-06 Fragment of wall</td>
<td>Wall surrounding a factory. Same location as KS-05 and KS-06</td>
<td>Mixture of brick and cement. Noticeably contaminated</td>
</tr>
<tr>
<td>KS-07 Fragment of wall</td>
<td>Factory wall over a dock</td>
<td>Algal presence. Higher algal presence and smoother surface in horizontal than in vertical side</td>
</tr>
</tbody>
</table>
matrix. An average layer depth of 547 $\mu$m with a 3.5% relative standard deviation was measured for the ten craters. As expected, the shape of this layer was uneven, but its average depth was in good agreement with the remote LIPS measurements showing an average relative error of about 8%.

Influence of sample-surface conditions

It is well known that the presence of water affects LIPS measurements. Owing to its high heat capacity and high latent heat of vaporization, water consumes a significant share of the laser pulse energy which, therefore, is no longer available for ablation and excitation of the actual sample. Consequently, LIP signal is reduced, having an immediate impact on analytical results. To quantify this effect, a stone fragment (KS-05) was analyzed under different conditions simulating those commonly found in the field. Three Cr depth profiles were measured, each of them being an average of ten individual depth profiles. To keep dispersion due to sample heterogeneity to a minimum, all crater positions were chosen to be in close vicinity in a apparently homogenous zone under a visual inspection. Fig. 3 shows the three resulting Cr depth profiles corresponding to the same sample under different conditions of humidity and surface salinity. The first depth profile was obtained from a dry sample. A 10 mm x 10 mm x 5 mm (l x w x d) slice of the sample surface was cut and then dried in a muffle at 80 °C for 1 day. The dust in the surface acquired a brown-grey color due to the lost of the natural humidity. Ten depth profiles were measured and averaged to produce the one shown in Fig. 3 labeled as (a). In a following experiment, the sample was damped in deionized water. Assuming that the amount of water diffused to the compact matrix is negligible, i.e. the higher amount is absorbed in the superficial dust, a surface water density of 53.4 mg cm$^{-2}$ was estimated by differential weighting. A new set of ten depth profiles was measured and averaged to produce the one shown in Fig. 3 labeled as (b). The sample was then dried and subsequently damped in a NaCl solution similar to that found in the sea (3.5% NaCl w/w). A surface density of 55.27 mg cm$^{-2}$ for the saline sample was now estimated. A last series of ten depth profiles was acquired and averaged to produce profile (c). By observing the figure, several features can be identified regarding the shape, the intensity maxima and the depth of the profiles. As for the former, the three profiles exhibit an initial intensity rise to reach a maximum after about two (a) to four (c) laser shots. A signal decay to a minimum is subsequently observed whose position in laser shot number varies from seven shots for profile (a) to about eleven shots for profile (c). A second maximum is then reached in the three profiles following the same sample order as described for the other features. Eventually, a steady behavior is found after a signal decrease for the remaining laser shots. These results reveal a higher ablation rate for dry samples than under the presence of humidity, whether saline or not. Such behavior agrees with expectations, i.e. the presence of water should constrain the available laser energy, thus lowering the ablation rate. However under moist conditions, the surface dust becomes more compact and this could favor a higher proportion of ablated material being ionized what would explain the higher intensity observed in profiles (b) and (c). In any case, the behaviour of the emission observed in this sample could differ from other samples with a more porous matrix.
Table 3 Summary of results extracted from the quantitative analysis of the superficial dust deposited over the samples

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Cr conc. (wt.%)</th>
<th>Number of shots</th>
<th>Estimated Cr depth/mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>KS-01</td>
<td>4.8</td>
<td>11</td>
<td>0.11</td>
</tr>
<tr>
<td>KS-02</td>
<td>13.3</td>
<td>3</td>
<td>0.03</td>
</tr>
<tr>
<td>KS-03</td>
<td>2.7</td>
<td>46</td>
<td>0.20</td>
</tr>
<tr>
<td>KS-04</td>
<td>1.4</td>
<td>17</td>
<td>0.48</td>
</tr>
<tr>
<td>KS-05</td>
<td>3.1</td>
<td>24</td>
<td>0.18</td>
</tr>
<tr>
<td>KS-06</td>
<td>5.5</td>
<td>24</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Three-dimensional analysis of composition

The great heterogeneity of environmental samples is one of the main drawbacks to achieve representative analytical results with laser ablation (LA) based techniques such as LIPS. For this reason, acquiring spatially-related information may result necessary to reach an accurate knowledge of sample composition. Topography of the samples often represents a major drawback for LA measurements since the depth of focus (DOF) is very short and the distance between the sample and the focussing optics must be tightly adjusted. Oppositely, remote LIPS overcomes this situation due to the longer DOF involved in these configurations. When it comes to environmental samples, such features of remote configurations offer the possibility of analysing a sample and delivering information about the spatial distribution of elements on its surface. For this experiment, a dock rock (KS-04) was analyzed. An area of 20 mm × 18 mm was scanned both across the surface and in depth to obtain a three-dimensional map of composition. The elements analyzed in this experiment were Cr, Fe, by the first pulses and evidences the ability of vegetation to trap and retain surface contamination. The Cr concentration measured for the latter sample, 13.3% in weight for the first laser pulse, is the highest value found. However, this result must be taken as an orientating figure as it falls outside the calibrated concentration range. Only three laser shots were necessary to extinguish the contamination layer.

In the case of the soil sample (KS-03), the Cr signal was also present although to a lower intensity than in vegetation samples. Despite this, Cr signal remained beyond 1500 laser pulses being still present in spectra acquired from its bottom surface. The 20-mm figure in Table 3 corresponds to sample thickness and is indicative of the high diffusivity of pollutants through this kind of porous and granulated samples. The lower Cr concentration measured in the first layers could be partly due to the dilution caused by diffusion towards the subsoil. A similar case is that of the dock rock (KS-04), which exhibits the lowest concentration of the whole set of samples whilst Cr remains detectable during 46 laser shots. The continuous cleaning and erosion of the surface by the sea water and the high porosity of the surface in this sample were found the main reasons for the lower Cr concentration in the surface and the thicker contaminated layer as compared to the other samples. KS-05 and KS-06 samples were taken from the same location, close to a factory, but their spectra reveal a higher Cr signal corresponding to a concentration of 5.5% in first layers, probably due to the higher proximity of this sample to the contamination source.

Quantitative analysis

Quantitative results were obtained by performing a calibration curve of Cr(i) emission at 520 nm normalized to Mg(i) 518 nm peak area using slag samples as standards. Suitability of the slag samples for this task was confirmed by X-ray diffractometry and X-ray fluorescence analysis. Analytical figures of merit are summarized in Table 2. To avoid possible measurements errors due to heterogeneities in the sample, ten different zones were studied in the surface of every sample and then the results were averaged. Although the matrix could be far different from sample to sample, only data corresponding to the dust layer in the sample surface was considered for analysis. Thus, the quantitative analysis reported is only an estimation of the amount of Cr contained in the dust deposited over the samples. Table 3 summarizes the Cr concentration estimated for all samples. The number of shots necessary to extinguish Cr signal was measured. The presence of Cr in the surface of bark (KS-01) and leave (KS-02) is significant in the layer removed

Table 2 Analytical figures of merit: LOD, limit of detection (3×SD/Slope). LDR, linear dynamic range. R, correlation coefficient. SD, standard deviation of the signal

<table>
<thead>
<tr>
<th>Element</th>
<th>λ/nm</th>
<th>Slope</th>
<th>R</th>
<th>LOD (wt.%)</th>
<th>LDR (wt.%)</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>520.45, 520.60, 520.84</td>
<td>0.1887</td>
<td>0.9876</td>
<td>0.21</td>
<td>1.1-6.7</td>
<td>0.013</td>
</tr>
<tr>
<td>Fe</td>
<td>489.15</td>
<td>0.0469</td>
<td>0.9198</td>
<td>0.19</td>
<td>0.6-1.7</td>
<td>0.003</td>
</tr>
</tbody>
</table>
Ca and Mg. A lateral and in-depth resolution of approximately 1.5 mm and 0.01 mm per laser shot was achieved, respectively. Fig. 5 illustrates the composition distribution for the cited elements. Each layer shown is separated ten pulses from each other, the uppermost corresponding to the sample surface. In the case of Cr and Fe, their depth profiles show the concentration (wt.%) while for Ca and Mg, the illustration shows the net intensity. In the left scale bar, the depth is shown in mm and above each graph, a graded colour scale represents the concentration or the signal intensity of each element. A photograph of the sampled area is also shown in the figure, where the topography of the sample and the dimensions of the analyzed zone can be observed. As illustrated, Cr and Fe concentrations decrease in depth in a parallel way. Ca intensity decreases in depth as well, but steeply for the first ten pulses –0.10 mm – the signal remaining constant as the sample matrix is reached. Mg behaviour is quite different than that of mentioned elements. As shown, the signal increases for the first ten pulses and then remains steady through the matrix. The high concentration of Cr and Fe in the first 20 pulses, 0.21 mm, is noticeable and this fact is indicative of the high degree of contamination deposited in the sample surface. The diffusion of these elements towards the sample matrix is significant in comparison to Ca, which exists in a higher concentration for the first 0.11 mm. The increase of Mg signal during the first shots shows the lower concentration of this element in the contamination layer in relation with the matrix.

Conclusions
Remote LIPS has been demonstrated as a suitable technique capable to deliver qualitative and quantitative information of the pollutants accumulated in environmental samples. Sample salinity and humidity have been shown to influence the measurement of surface contamination. Remote LIPS has been used to measure the level of the pollutants deposited in a sample and to associate the concentration measured to the sample orientation and to the surrounding environment. Relying on the longer depth of focus found in these remote configurations, the potential of remote LIPS for three-dimensional analysis of composition of a sample with independence of its topography has been demonstrated.

Acknowledgements
This work was partially supported by Project BQU2001-1854 of the Ministerio de Ciencia y Tecnología of Spain. One of the authors (CLM) wants to thank the Spanish Ministerio de Ciencia y Tecnología for a research fellowship.

References