The capability of laser-induced breakdown spectrometry (LIBS) to resolve complex depth profiles is demonstrated. Electrolytically deposited brass samples were analyzed by monitoring the emission corresponding to Cr (357.8 nm), Ni (341.4 nm), Cu (327.4 nm) and Zn (334.5 nm). The nominal thickness of the layers was known, which permitted an estimate of the ablated mass in the range between 150 and 500 nm per pulse depending on the matrix and laser irradiance. Laser irradiance was varied by defocusing, and its effect on the depth-resolution of LIBS was tested. For comparison purposes, a commercial zinc-coated steel was also studied by following the Zn and Fe emission intensity depth profiles with a commercial glow-discharge optical emission spectrometry system to obtain information on the exact location of the Zn–Fe interface (12 μm). The ablation rate in terms of ablated mass per pulse was found to be at the ng per pulse level and depended on the laser pulse irradiance.

Keywords: Laser-induced breakdown spectrometry; depth-profile analysis; laser plasma

The day-to-day requirements of industry demand the accurate determination of the elemental composition of a sample (bulk analysis) as well as an exact location of the interfaces and the study of concentration gradients (space-resolved microanalysis). The simple description of the amount and quality of a material is as important as the knowledge about the spatial distribution of the components in both two and three dimensions. The composition of each individual layer, particularly at the interface, which is available from a depth profile, is much more informative than the composition of one depth or the average over a range of depths. In this sense, spectrochemical techniques with high-spatial resolution are powerful tools for the analytical chemist.

Analytical techniques for bulk elemental determination are unable to provide complete information on the spatial composition of non-homogeneous samples as their dissolution is a prior step to the analysis. The only exception is the use of ablation cells in ICP, where the solid sample is irradiated with a focused laser beam to vaporize a small amount of material that is carried with the help of an argon flow to the torch. However, it is difficult to obtain steady signals as the sample introduction is pulsed. On the other hand, as a high laser repetition rate is required to obtain the analytical signal, in most instances the depth dimension is lost.

Development of new microanalytical techniques with lateral and depth resolution capabilities is a must in modern chemical analysis. Several surface analysis techniques are very mature (e.g., SIMS and X-ray photon spectroscopy) and show extremely high capabilities to perform surface and interface analysis at the atomic level. However, this resolution reduces their field of application to semiconductor technologies, thin films analysis, surface catalytic processes and other chemical problems restricted to the first few atomic layers.

However, most practical situations do not demand such extreme levels of resolution. Analysis within a time-frame compatible with industrial requirements and applicability to routine analysis or industrial applications beyond laboratory-scale work are desirable. In this sense, glow-discharge optical emission spectrometry (GD-OES) and laser-induced breakdown spectrometry (LIBS) are being introduced for the cited purposes owing to their multi-elemental capability, lower cost, the simplicity of working at atmospheric or moderately low pressure and the ability to detect major and minor components in a great variety of matrices. The main disadvantage of GD-OES and LIBS is the degree of standardization needed with respect to the quantification problem. Several groups have developed different mathematical algorithms for the quantification of concentrations and sputtered depth in GD, that have been incorporated in the software of commercial apparatus. In addition, the GD process allows an almost-flat profile in the sputtered sample, resulting in a better resolution for depth profile purposes. In contrast, the laser-ablated crater shows different shapes and depths as a function of the characteristics of both the sample (thermal conductivity, density) and the laser beam (wavelength, pulse length, temporal mode). However, the lateral resolution in GD, limited by the diameter of the anode disc, ranges between 0.5 and 4 mm, while lateral resolutions of a few micrometres have been described in microanalytical applications using a Nd:YAG laser.

The generation of laser-produced plasmas and their further spectral analysis has been known since the development of the first laser devices and the analytical applications have been widely discussed in several books, reviews and original papers showing several applications in different fields such as geochemistry, materials characterization and environmental studies. In spite of this, the laser–matter interaction is a complex process that is not yet completely understood. This term involves the coupling of the energy into a solid, resulting in vaporization; atomization; ionization; formation of molecules and fragments; shock waves; plasma initiation and expansion; and a hybrid of these and other processes. All these processes influence the ablation rate when depth analysis is to be performed. In the present work, some data on the capability of LIBS to perform depth analysis are presented. Although LIBS has been widely used for direct chemical microanalysis of solid samples, few papers deal with the quantification of depth resolution of a LIBS system. For this purpose, different electrochemically prepared samples were analyzed as well as a zinc-coated steel. A pulsed Nd:YAG laser was fired repetitively at a single site to erode the coating and then ablate the substrate. The laser-induced plasma from each laser shot was monitored by a gated charge-coupled device (CCD) detector to yield an emission–wavelength–time signature, i.e., depth profile.

EXPERIMENTAL

Apparatus

A detailed description of the system has been given elsewhere, and only minor comments will be given. A summary of the
system and some specifications are presented in Table 1. The second harmonic of a pulsed Nd: YAG laser was used to irradiate the samples, guiding the beam with glass prisms. The laser beam was focused onto the sample surface using a planoconvex lens with a focal length of 100 mm and f-number of 4. Optical collection was performed with a 100 mm focal length biconvex quartz lens. An optical magnification of about 1:1 was used throughout. The laser-ablated plasma emission was collected onto the entrance slit of a 0.5 m focal length imaging spectrograph. Typically, the entrance slit was set at 20 µm.

Detection of the plasma light was monitored with an intensified CCD. Calibration was conducted with a mercury pen lamp or by registering the spectra of different pure metals and known alloys. Operation of the detector was controlled with 4Spec 1.20 software. The detector was equipped with a microchannel plate (MCP) image intensifier controlled via an RS 232 serial port. In order to obtain a precise trigger signal, a fast photodiode viewing split portion of the beam was used instead of the SYNC output signal of the laser. Care was also taken to avoid electrical coupling between the laser and the photodiode.

Samples

Samples consisted of a commercial brass (typically a Zn–Cu alloy with minor percentages of different elements). Copper, nickel and chrome platings were deposited following an electrochemical process. The samples were set in different baths to obtain the multilayered sample. No details of the process (reactants, pH, current and time) were given by the manufacturer (Dimauluz, Málag, Spain). From the base to the surface, the sample consists of a brass foil, two different copper layers (acid and alkaline), a nickel layer and a chromium layer. The depth of each layer was stated to be 2 µm. In order to obtain information about the sample, the signals corresponding to Cr (357.8 nm), Ni (341.4 nm), Cu (327.4 nm) and Zn (334.5 nm) were simultaneously monitored as a function of the laser shots (or time, as the acquisition frequency was previously fixed) with the use of a 1200 grooves mm⁻¹ diffraction grating. As Cu is present in both the brass base and the subsequent Cu layer, the Zn signal was monitored as an indication of the complete depletion of the deposited layers. A zinc-coated steel was also used for comparison purposes. In this case, the signals corresponding to Zn (328.23 nm) and Fe (328.67 nm) were recorded and processed in a similar manner.

RESULTS AND DISCUSSION

To date, there are no models that completely describe the laser–matter interaction processes, although it is clear that laser irradiance (energy density) and the physical properties of the material to be analyzed (heat transfer coefficient, reflectivity, etc.) are important. In a general sense, two different processes can be described as a function of the laser irradiance, vaporization and ablation. Laser pulse duration and optical properties (absorption and reflection) of the sample determine both the fraction of the incident power that it is absorbed and the depth of optical absorption within the sample. When the irradiance reaches the ablation threshold, the surface temperature is instantaneously raised above the vaporization temperature, producing a typical ablation crater. It must be taken into account that the distinction between power densities for vaporization and ablation is approximate and matrix-dependent, and power densities in a broad range between 10⁶ and 10¹⁰ W cm⁻² can cause vaporization and/or ablation, and additional processes not yet identified, depending on the sample.

With the sample and laser source fixed, the geometrical characteristics of the formed crater in LIBS depend on the laser irradiance. For a given energy per pulse, if the lens-to-sample distance corresponds to the focal point of the lens, the ablation crater is significantly deeper than when the beam is defocused. The latter focal geometry is the best choice when a better depth resolution is required. The erosion (ablated) rate in LIBS, that is, the amount of sample eroded per unit of time or pulse, is fairly high compared with other surface techniques, such as SIMS, so that depth profiling of relatively thick layers (>1 µm) or coatings on metal substrates can be performed rapidly. In order to calculate the effect of defocusing in the ablation crater area, the laser energy was set to its minimum (30 mJ) by decreasing the flash lamp energy. The laser was fired over the sample at different lens-to-sample distances from the focal point (where the irradiance is maximum) in 1 mm steps. A plot of the theoretical spot area and found crater area versus the laser irradiance is represented in Fig. 1. As shown, defocusing of the laser beam allows the laser irradiance to be decreased by one order of magnitude, which may permit a better depth resolution.

In order to study the effect of laser irradiance on depth resolution, the Zn emission line at 334.5 nm was monitored versus the number of laser shots using the electrochemically prepared samples. The Zn signal was chosen as an indication of the number of laser shots required to deplete completely the different deposited layers independently of the expected different ablated rates caused by the non-homogeneous composition of the samples. The number of shots required was monitored as a function of the irradiance. For this purpose, the sample surface was placed at the focal point (irradiance equal to 17 GW cm⁻²), and 1 and 2 mm below the focal point (corresponding to irradiance values of 9.5 and 7.5 GW cm⁻², respectively). For the cited irradiances, 14, 20 and 53 laser shots were required before the appearance of the Zn signal.

![Figure 1](https://example.com/fig1.png)
The depth capabilities of LIBS were tested by following the emission profiles of Cu, Zn, Ni and Cr with the number of laser shots in the multilayered sample. As a compromise between intensity and depth resolution, the laser energy was fixed at 40 mJ, three laser shots were averaged for each data point, and the laser was defocused by placing the sample 5 mm below the focal point. The results are shown in Fig. 2. To give an idea of the time required for the analysis, a time axis is also shown, which was calculated from the laser repetition rate used (1.25 Hz). As shown, the intensity profile corresponds exactly to the spatial pattern of the sample (Cr, Ni, Cu and Zn from outer to inner layer as described under Experimental). Although the laser energy is higher, the enlargement of the beam size and hence the decrease in the irradiance value, is sufficient to permit the firing of 500 laser shots after the appearance of the Zn signal.

In order to carry out a more precise study of the outer Cr–Ni layer, a one-shot-per-memory experiment was performed at two different laser irradiances, instead of storing different laser shots in a single memory. The laser energy was set to a minimum to permit a better resolution. The result is shown in Fig. 3. As can be seen, there is an acute difference in the number of shots required to reach the interface. While five shots are sufficient at higher irradiance, 12 shots are needed to reach the same depth in the second case. Knowing the depth of the layer, it was possible to calculate the ablation rate in eroded nanometres per laser shot. The results of irradiance used, laser shots and ablation rate are shown in Table 2.

For the sake of comparison, a galvanized steel was studied following the profile of the Zn I 328.23 nm and Fe I 328.67 nm emission lines using the LIBS system and a commercial direct-current GD-OES system. The results of the depth profiles of the sample processed by LIBS at two different laser irradiances (5.5 and 5 GW cm$^{-2}$) and by GD-OES are shown in Fig. 4. As can be seen, the GD-OES data indicate that the Zn–Fe interface is located at about 12 μm below the sample surface, showing a diffusion zone ranging from 10 to 14 μm. The results of LIBS in terms of laser irradiance, number of shots required to reach the interface and ablation rate are summarized in Table 2. The interface is reached after 25 pulses at an irradiance of 5.5 GW cm$^{-2}$, while 75 shots are required when the irradiance is decreased to 5 GW cm$^{-2}$. Assuming a similar ablation rate up to the point at which the interface is reached, the ablation rate per pulse can be estimated to be 560 nm per pulse in the first case, and 185 nm per pulse in the second. After a comparison with the results obtained from the Cr–Ni interface, similar irradiance regimes imply different ablation rates as a function of the matrix-dependence of the laser ablation process. As shown, at 5.5 GW cm$^{-2}$, the ablation rate is 160 nm per pulse for the Cr–Ni matrix, while the rate is 3.5 times higher for the galvanized steel. The explanation of this fact must be related to matrix effects and the physical properties of the sample (reflectivity at the laser wavelength, thermal conductivity coefficients), although further studies involving the use of high-purity metals in the layered sample would be required. However, this phenomenon has previously been observed.

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Laser irradiance/ GW cm$^{-2}$</th>
<th>Laser shots</th>
<th>Ablation depth/ nm per pulse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr–Ni</td>
<td>7.2/5.5</td>
<td>5/12</td>
<td>400/160</td>
</tr>
<tr>
<td>Zn–Fe</td>
<td>5.5/5</td>
<td>25/75</td>
<td>560/185</td>
</tr>
</tbody>
</table>

![Fig. 2](image2.jpg) Variation of emission profiles of Cr, Ni, Cu and Zn lines with depth. For explanation of sample structure and experimental conditions see text.

![Fig. 3](image3.jpg) Depth-profile detail of a Cr–Ni interface in the sample studied in Fig. 2. As shown, an increase in irradiance has a critical effect on the number of laser shots required to reach the interface. Cr (broken line), Ni (solid line).

![Fig. 4](image4.jpg) Emission profile of Zn (solid line) and Fe (broken line) in a zinc-coated steel studied by LIBS at two different laser irradiances and by GD-OES. For details see text.
studied in other techniques such as GD, where there is a strong dependence of the sputtering rate on the experimental conditions (in this case, the current intensity and applied voltage), and some good approaches can be found.\textsuperscript{18}

The amount of ablated mass per pulse was also estimated. In order to avoid the effect of different matrices on the ablation rate, the experiments were carried out with a commercial brass sample that was cut into small pieces weighing about 10–100 $\mu$g. A plot of the amount of lost (ablated) mass after 250, 500 and 1500 laser shots is shown in Fig. 5. The experiment was performed at two different irradiances, 17 and 7 GW cm$^{-2}$. The correlation coefficients were 0.987 and 0.998, respectively. From the slopes of the fitting lines, ablation rates of 11.5 and 6.3 ng per pulse were obtained, respectively.

**CONCLUSIONS**

It has been shown that LIBS is a technique with promising capabilities for depth-profiling analyses. Ablation depths of 6.5 ng per pulse have been obtained, which imply absolute limits of detection of the order of fg per pulse for an element present in the sample at a concentration of a few ppm. However, the laser–matter interaction processes, which are not well understood, limit the applicability of the technique. Differences in the ablation depth due to matrix effects have been observed in the resolution of a Cr–Ni and Cr–Fe interface using similar experimental conditions. Also, a comparative study using GD and LIBS at different irradiances has been carried out, demonstrating a good agreement between both techniques, although a better resolution at the interface is obtained with GD owing to the differences in the shape of the craters produced. However, we believe that further studies on the focusing step (spatial filtering of the beam, use of achromatic optics) and a precise control of the energy distribution in the laser beam would yield significant improvements in the depth profiling capabilities of the technique.

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**REFERENCES**