Analysis by laser-induced breakdown spectroscopy of complex solids, liquids, and powders with an echelle spectrometer

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One of the most promising approaches to laser-induced breakdown spectroscopy (LIBS) experiments involves the use of an echelle spectrometer coupled with an intensified CCD. Even if drawbacks remain with its use, the echelle spectrometer facilitates a multielemental analysis that is more rapid than can be obtained with the more-conventional Czerny–Turner spectrometer and, moreover, does not sacrifice reliability. Quantitative results obtained with such apparatus for solids, liquids, powders, and gases are described and when possible compared with results from Czerny–Turner spectrometers. Liquid analysis by LIBS with echelle spectrometers has allowed a spectral database to be compiled. Once the qualitative spectra of pure elements in aqueous solutions, are obtained, they can be used for qualitative analysis of unknown samples. © 2003 Optical Society of America

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1. Introduction

In recent years laser-induced breakdown spectroscopy (LIBS) has been studied because of the numerous advantages of its use in remote analysis in various environments, including hostile ones. As an example, a recent paper mentions the use of LIBS to characterize solids submerged in water. Moreover, in this paper applications of LIBS to control the cooling systems of nuclear plants are proposed. Experiments seem to indicate that LIBS will have important applications in nuclear waste control. But all these applications require not only a qualitative but also a quantitative rapid multielemental analysis, which implies a large spectral coverage with high resolution. Of course, high spectral resolution can be obtained with conventional Czerny–Turner spectrometers but only in a restricted portion of the spectrum. It takes many laser shots and therefore much time to make the sequential measurements that are needed for the analysis of many elements.

In contrast, in recent years an echelle spectrometer combined with an intensified CCD camera has offered a large spectral domain for investigation.

The objective of the research described in this paper is to highlight the great potential of echelle spectrographs not only for qualitative analysis but also for quantitative analysis. To our knowledge, there are three commercial apparatuses relevant to LIBS analysis. Our aim in this paper is not to compare all these systems but to give examples of ways in which an echelle spectrometer can be an interesting system.

Early in the recent development of echelle spectrometers for LIBS analysis, Bauer et al. tried to connect an echelle spectrometer and a Princeton Instruments intensified CCD camera. Al and Fe spectra were produced, but to obtain large spectral coverage with this first apparatus, they used a mobile mirror inside the device. The same problem was encountered by Haisch et al., who developed an echelle spectrometer for analysis of colloid materials. These early publications reveal that a large intensified CCD camera is necessary for important spectral coverage without any moving components. At the same time, Lindblom presented a glass spectrum obtained with his new echelle spectrometer (the Mechelle spectrometer). Large spectral coverage [190 nm, 1100 nm] with no gaps illustrates the wide applicability of echelle spectrometers. Recently a versatile spectrometer was proposed by Florek et al.
In parallel with the development of the apparatus, with a multichannel Mechelle 7500 commercial instrument,11 Goode et al. showed an interesting ability to classify quickly and qualitatively various alloys, taking into account the entire emission spectrum and using a principal-component analysis. Almost the same time, another application was described by Fink et al.12 They obtained good results from a LIBS experiment that included an echelle spectrometer (Model ESA 3000, LLA GmbH, Berlin) to investigate recycled thermoplasts.

The LIBS technique is known as a destructive analytical method. But Bicchieri et al.13 applied the technique in research with a medieval manuscript because of its utility in terms of depth resolution and local analysis. Therefore the Mechelle 7500 spectrometer was useful for simultaneous multielement analysis and production of significant amounts of information.

Recently, applications of LIBS to liquids,14,15 wood,16 aluminum alloys,17 glass,18 and geological samples19,20 have been described, proving the existence of a growing interest in echelle spectrometers.

At the same time, some developments of large broadband optical range spectrometers have also been described.21–25 These new applications which use Ocean Optics (Dunedin, Fla.) miniature spectrometers, highlight the necessity to collect as much information as possible after plasma formation to develop powerful analytical applications of LIBS.

The goal of the present research was to determine whether LIBS experiments that use echelle spectrometers are appropriate for a variety of applications: investigations of liquids, powders, solids, and gases. We built homemade software with which to identify automatically various emission lines among the huge quantity of data produced by the system. As a consequence, a library of LIBS spectra was obtained for 46 elements and used to investigate unknown samples.

2. Experimental Setup

For each application described below a standard LIBS experiment was built. A Nd:YAG laser (Quantel Brilliant B) operating at 532 nm was used as the ablation source, with an energy of 60 mJ/pulse. Three reflective mirrors guided the laser to a focusing lens. The closest mirror to the lens, made from quartz that is reflective at 45°, permitted plasma recording in the same direction. The laser beam was focused by a plano–convex quartz lens with a different focal length for each application (for liquids, f = 30 cm; for powders, f = 50 cm; for solids and gases, f = 10 cm). For liquids and powders longer focal lengths were chosen to prevent splashing from damaging the optics during the experiment, and the laser frequency was fixed at 1 instead of 10 Hz (for solid and gas applications). Only for liquid applications was the laser’s optical pathway tilted at an angle of 15° for the same reason, which is described in detail in Ref. 14. For gas applications an airtight chamber was designed with one quartz window to guide the laser inside and to collect the plasma emission in the same direction.

Once the plasma was formed, its emission went through the laser focusing lens and the quartz dichroic mirror and was then focused onto a 1-m-long fused-silica optical fiber (numerical aperture, 0.22; core, 1 mm) placed behind the quartz mirror closest to the lens. As an example, the experimental setup used for investigations of liquids is presented schematically in Fig. 1. This setup is described in full detail in Ref. 14.

For some experiments described below, the plasma emission was imaged at the entrance slit of a Czerny–Turner spectrometer (Jobin Yvon Model THR 1000, Longjumeau, France; not shown in Fig. 1) or at the entrance of an echelle spectrometer. The ESA 3000EV spectrometer (LLA GmbH, Berlin, Germany) was used for liquids, solids, and powders (its spectral range is 200–780 nm and its resolution is λ/Δλ ≈ 10,000). For gases a Catalina SE 200 (high order version, Catalina Scientific Corporation, Tucson, Arizona) echelle spectrometer provided spectra (its spectral range is 190–1100 nm and resolution is λ/Δλ ≈ 3,000).

3. Results and Discussion

A. Echelle Spectrometer for Investigations of Liquids

Even if LIBS analytical applications to liquids were studied less frequently than those to solids, standard sample preparations are obviously much easier. The solutions used for this study were purchased from the Spex Certiprep Company (Metuchen, New Jersey). With several mono elemental solutions chosen at concentrations of 10,000 µg ml⁻¹, the corresponding spectra were obtained with the echelle spectrometer detector. The echelle spectrometer produced a huge quantity of data, an outcome that first was considered a drawback; therefore
homemade software (VISUAL BASIC 6.0, Microsoft) was written to extract automatically the various emission lines of interest and to accumulate the spectral database obtained by LIBS. So far, LIBS spectra for 46 elements have been gathered in our spectral database. As an example, some of the results obtained for Co are compared in Table 1 with those that we extracted from Ref. 26. The echelle spectrometer is reliable in terms of wavelength calibration because the difference between the National Institute of Technology (NIST) database and the experimental data was found for Co and also for the other elements to be \( \pm 15 \) pm. Because there are no moving parts in the echelle spectrometer, automatic wavelength calibration is a great advantage for qualitative and obviously for quantitative application. We have used this spectral database built for LIBS experiments to interpret unknown spectra. Examples are provided for investigation of powders.

After several tests for wavelength calibration, quantitative studies of liquids were performed by dilution of known quantities of standard solutions in distilled water. The ability of an echelle spectrometer (see Fig. 2 for an example showing a calibration curve for Na in water; the detection limit was 0.55 \( \mu g \) \( ml^{-1} \)) to give quantitative results was assessed. Each datum of the calibration curve represents the mean value of six duplicate experiments. Each measurement corresponds to the area of the emission line of interest obtained with an accumulation on the detector of 300 laser shots. The reproducibility of each point in the calibration curve was 5–10%. The accuracy of the analysis was evaluated to be \( \sim 10\% \), assuming that the unknown concentration is far from the detection limit and of course within the limits of the calibration curve. The sensitivity of such system has also to be evaluated by direct comparison of the detection limits obtained in the same conditions (laser energy and experimental setup) with a classic Czerny–Turner spectrometer (see particularly Ref. 14, which described the same experimental setup).

A direct comparison of all the essential parameters (gate delay, gate width, gain of the camera) remains difficult. Therefore for the limits of detection (LOD) obtained with the echelle and the Czerny–Turner systems we must admit that optimum parameters were chosen. Table 2 shows the different limits of detection obtained for Na and Mg in the research reported here and that reported previously in the literature. For Mg the result that we obtained has the lowest LOD, only Ref. 27 presents a better LOD for Na. With these results we can conclude that detection limits obtained with an echelle spectrometer are of the same order of magnitude as those obtained with a Czerny–Turner spectrometer.

The possibility of using systematically an internal standard that can have an emission line that is not close to the element of interest is also an essential feature of the echelle spectrometer. This opportunity, very often used for inductively coupled plasma optical emission spectroscopy, can be important to be used to improve the stability of the system with time (reproducibility). In Fig. 3, two calibration curves are shown as examples of calibration curves of Ba in

<table>
<thead>
<tr>
<th>Co LIBS Spectral Database</th>
<th>NIST Spectral Dataa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength (nm)</td>
<td>Intensity (a.u.)</td>
</tr>
<tr>
<td>345.344</td>
<td>41,128</td>
</tr>
<tr>
<td>340.505</td>
<td>28,341</td>
</tr>
<tr>
<td>356.931</td>
<td>26,178</td>
</tr>
<tr>
<td>352.981</td>
<td>23,716</td>
</tr>
<tr>
<td>350.626</td>
<td>21,636</td>
</tr>
<tr>
<td>358.717</td>
<td>19,932</td>
</tr>
<tr>
<td>350.222</td>
<td>19,069</td>
</tr>
</tbody>
</table>

aRef. 26.

The source in all cases was Co I.

Fig. 2. Calibration curve of Na in an aqueous solution obtained with an echelle spectrometer (equation of the line, \( y = 1899x + 3831; R^2 = 0.9983 \)).
aqueous solutions with and without Sc as an internal standard. The experimental parameters used for Na were kept constant for the Ba study. We are not aware of any previous studies of the time evolution of the calibration curve. With the results shown in Fig. 3 our conclusion is that no improvement was achieved by the use of an internal standard. The reliability of the LIBS technique for the analysis of liquids is under study, and thus the usefulness of an internal standard will have to be proved.

B. Echelle Spectrometer for Analysis of Solids
Having established the utility of an echelle spectrometer for the analysis of liquids, we also employed the detector for analysis of Al alloys. This apparatus was an interesting choice for recording and choosing the most sensitive lines for various trace elements to be analyzed but also for the less-sensitive lines of the matrix. The matrix lines can be used as internal standards in the calibration curves of trace elements if no saturation or self-absorption occurs. With different Al alloys, 12 calibration curves were obtained by LIBS. Each datum obtained for the calibration curve corresponds to five duplicate experiments at different positions on the sample surface to prevent potential sample inhomogeneity. Two hundred laser shots were accumulated on the detector. The same reproducibility and accuracy were found for applications to solids and to liquids. An example of a calibration curve for Ni is shown in Fig. 4. The detection limits are close to those that can be found in the literature, but obviously all trace elements can be investigated at the same time and thus quickly. Ta-

Table 2. Limits of Detection (μg ml⁻¹) of Na and Mg in Water

<table>
<thead>
<tr>
<th>Element</th>
<th>Present Work (Echelle)</th>
<th>LOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.4</td>
<td>1</td>
</tr>
<tr>
<td>Na</td>
<td>0.55</td>
<td>1</td>
</tr>
</tbody>
</table>

aRef. 15.
bRef. 14.
cRef. 27.

Fig. 3. Calibration curves, with (detection limit, 0.3 μg/ml; equation of the line, \( y = 0.12x + 0.15, R^2 = 1 \)) and without (detection limit, 0.36 μg/ml; equation of the line, \( y = 6093x + 8455, R^2 = 1 \)) Sc as an internal standard, for Ba in an aqueous solution obtained with an echelle spectrometer.

Fig. 4. Calibration curve obtained for Ni in Al alloys (equation of the line, \( y = 19.3x + 0.3, R^2 = 0.99 \)).
Table 3. Detection Limits Obtained for Trace Elements in Al Alloys\(^a\)

<table>
<thead>
<tr>
<th>Element</th>
<th>This work ((\mu g \cdot g^{-1}))</th>
<th>Ref. 17 (ppm)</th>
<th>Ref. 28 (ppm)</th>
<th>Ref. 29 (ppm)</th>
<th>Ref. 30 (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>4</td>
<td>1.6</td>
<td>0.3</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cr</td>
<td>2</td>
<td>–</td>
<td>–</td>
<td>3</td>
<td>–</td>
</tr>
<tr>
<td>Cu</td>
<td>2</td>
<td>33</td>
<td>10</td>
<td>56</td>
<td>10</td>
</tr>
<tr>
<td>Fe</td>
<td>9</td>
<td>–</td>
<td>–</td>
<td>30</td>
<td>–</td>
</tr>
<tr>
<td>Mg</td>
<td>0.134</td>
<td>9</td>
<td>0.5</td>
<td>7</td>
<td>0.5</td>
</tr>
<tr>
<td>Mn</td>
<td>2</td>
<td>65</td>
<td>7</td>
<td>90</td>
<td>2</td>
</tr>
<tr>
<td>Ni</td>
<td>7</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Pb</td>
<td>15</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Si</td>
<td>10</td>
<td>90</td>
<td>14</td>
<td>–</td>
<td>14</td>
</tr>
<tr>
<td>Ti</td>
<td>3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>Zn</td>
<td>15</td>
<td>–</td>
<td>–</td>
<td>38</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^a\)A dash means no data available; ppm means parts in 10\(^6\).

Table 3 lists not only our results but also those reported in the literature. The type of spectrometer is specified for each reference. The values obtained for Cu, Mg, Si, Fe, and Zn are the lowest. The LOD reported in Ref. 17 for Be with a Czerny–Turner spectrometer is better than that obtained with the two-echelle apparatus. This result can be due to the sensitivity of the various detectors to a specific wavelength. For Cr and Mn, detection limits obtained with the two systems are similar. For Ni, Pb, and Ti no other values have been published to our knowledge.

C. Echelle Spectrometer for Analysis of Powders

Because LIBS instruments can be portable, applications to the screening of various soils can be interesting. A goal of our experiment was to show the capability of the echelle spectrometer for qualitative analysis of unknown samples. A spectrum was obtained with our standard LIBS experimental setup. Homemade software was built to extract the different emission lines of the experimental spectrum. Once they were obtained, all the wavelengths of the emission lines were automatically compared to our LIBS spectral database obtained with liquids and described above.

The intensities of the emission lines were also considered in our interpretation of the results. Observation of the three main lines in the experimental spectrum, as reported in the spectral database, is the criterion chosen for our calculation. Obviously the three main lines in the LIBS spectra of solids and liquids may be different, but generally lines that are sensitive for liquids are sensitive for solids. With this criterion, and only for a 1-s calculation duration, the elements Si, Fe, Mg, Ti, Ca, Na, Mn, Sr, Ba, O, and Cr were qualitatively observed in the unknown sample. For example, Fig. 5 shows a qualitative comparison of the lines observed with 10,000 \(\mu g/\text{ml}\) of Ti in water (reference spectrum) and those recorded for the soil sample. A quantitative interpretation of the results is more difficult, but use of an echelle spectrometer detector for a LIBS experiment is a powerful apparatus just for qualitative analysis.

D. Echelle Spectrometer for Control of Gases

In the present study an echelle spectrometer (the Catalina SE 200) was tested for control of gases. A mixture of 5% Kr in N\(_2\) was detected, a portion of the spectrum is depicted in Fig. 6. Other gas lines such as Xe(529.222 nm) and O(777.194 nm) were also observed with our experimental setup. We have performed no quantitative analysis for this gas study.
4. Conclusions
For several analytical applications of laser-induced breakdown spectroscopy to liquids, solids, powders, and gases, the use of a spectrometer that possesses a wide spectral range and particularly of an echelle spectrometer is an attractive choice.

Because a large portion of the spectrum is investigated simultaneously, many elements can be qualitatively and quantitatively studied at the same time. No moving parts could be found in the echelle spectrometers tested, which ensures stable wavelength calibration. Moreover, the difference between our database and the NIST spectral database for emission spectroscopy was ±15 pm.

The quantitative results described for liquids and solids are quite similar to those that have been reported in the literature for systems that use a standard Czerny–Turner apparatus. The main difference lies in the fact that fewer experiments are necessary for multielemental analysis to produce similar results. All the trace elements were investigated at the same time.

Because it is easy to find commercial pure monoelemental solutions of many elements, a spectral database dedicated to the LIBS technique was easily produced with the echelle spectrometer for 46 different elements. With criteria such as the presence or lack of sensitive lines, the spectral database can be used to analyze qualitatively unknown samples.

References


