Pencil lead scratches on steel surfaces as a substrate for LIBS analysis of dissolved salts in liquids

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Abstract. A new substrate for the quantitative analysis of salts dissolved in liquids with Laser-induced Breakdown Spectroscopy (LIBS) is introduced for the first time. A steel surface scratched with HB pencil lead is introduced as a very efficient and sensitive substrate for quantitative analysis of dissolved salts in liquids. In this work we demonstrate the analytical quality of this system with the analysis of the crystalline deposits formed by the dried aqueous solutions of salts. We focused on analytical parameters such as sensitivity and linearity for the salt cations in each case. Four salts were studied (Sr(NO3)2, LiSO4, RbCl and BaCl), at nine different concentrations each. To improve linearity and lower the overall error in the calibration curves, we introduce a novel outlier removal method that takes into account the homogeneity of the dry deposits on the analytical surface.

1. Introduction
LIBS (Laser-induced Breakdown Spectroscopy), is a frequently used tool for qualitative and quantitative analysis of solids, liquids, and gaseous substances of varying chemical composition. The LIBS technique provides information about the identity and concentration of the atoms present in a compound [1-4]. This technique uses a high intensity laser pulse focused on the sample to produce hot plasma which contains single atomic species representative of the sample composition. The high temperatures inside the plasma excite the atomic species present, which then emit light with unique spectral characteristics that permit identifying them. Furthermore, under the right conditions, the intensity of these spectral lines allows the determination of the concentration of the corresponding chemical species. With time, the overall spectral profile generated in LIBS changes from its initial creation. During the first few nanoseconds, the spectrum is basically a continuous background of incoherent radiation produced by the electrons moving away from the plasma. As time goes, the plasma cools down and the recombination of electrons and ions produces neutral atomic species. At this point, the spectrum begins to show spectral lines of those atomic species [3-14].

Although the analysis of solids by LIBS is very straightforward, the analysis of liquids presents difficulties due to fast light quenching, sputtering from the surface, among other things. Several approaches have been reported in the literature to deal with this problem [15-18]. Interestingly, Randall et al. used LIBS to analyze the elementary composition of liquids which were left, from spectra taken from...
the crystallites deposited on a suitable surface [19]. They demonstrated the possibility of analyzing nitrates or chloride salts dissolved in water using an amorphous graphite substrate (carbon disks), with good analytical performance [15-19].

Concerning this method, an important consideration is whether the solid crystals deposited on the surface reflect the actual stoichiometry present in the original solution. It was argued that for this to be so, it is necessary that the drying process will form a homogenous layer and that the evaporation of the solvent proceeds under such conditions as to assure no loses of the initial components. In this study, the role of the supporting substrate used was deemed important but was not studied systematically.

In a previous study, we used the same idea for liquid analysis and focused on the comparison of different substrates as analytical surfaces. As compared to graphite, the analytical performances of some of them were good. Of particular interest, in this report we will introduce for the first time a substrate for LIBS analysis of salts dissolved in liquids which is cheap, easy to use, and has good analytical characteristics, which is a steel surface scratched with a HB pencil. The results of the analysis by deposition of aqueous solutions of 4 different salts (BaCl₂, Sr(NO₃)₂, LiSO₄, RbCl) will be discussed. With regard to the quantification capabilities for LIBS analysis of this substrate we will show calibration curves for some different species. With this method we found that the limit of detection for the cationic component of all salts studied was below 1 ppm which was the arbitrary lower concentration we studied. In all spectra we were able of obtaining a good signal to noise ratio.

This kind of substrate for analytical purposes has been used also previously in a different field. Steel surfaces scratched with a HB pencil were used in Laser Desorption/Ionization in mass spectrometry, for analysis of small molecules. It has been shown that substrates generated with pencils of high blackness, such as 2B and 6B, perform well in this technique [20-22]. It must be noted that the typical laser fluence values of LDI and LIBS differ by orders of magnitude, and that consequently the analytical requirements of these techniques might be considerably different. Still, a common denominator in both cases could be that the high hydrophobicity of the scratched surface provides an efficient manner to produced highly homogeneous and small spot samples which collects suitably the dried material. That is, the small drop of water can dry forming a homogeneous distribution on the substrate [20-22].

The surface scratched with a HB pencil is highly hydrophobic because the typical components of pencil lead consist of the non polar compounds clay and wax [20].

2. Experimental Design

The equipment used in this study is a LIBS spectrometer 2000+ of Ocean Optics Inc. (Dunedin, Fl, USA) with range between (200-1100 nm) and resolution (λ=2nm). The system consist of a Laser Nd:YAG emitting up to 250 mJ in 10 ns pulses, a focusing lens, and an analysis chamber. The software used for the analysis was that provide by the fabricant, OOLIBS. In figure 1 a scheme of the setup used is shown [23].
2.1. Sample preparation
On all cases we deposited (1µl) of the salt solutions with an Eppendorf micropipette. The solution was then allowed to dry under a gentle stream of warm air. The resulting spots were approximately 1 mm in diameter. Prior to use, all steel surfaces were cleaned with de-ionized water. The same cleaning procedure can be used on the pencil-scratched substrates, but we preferred polishing the steel surface with 1200 polishing paper to eliminate all traces of the pencil layer should the substrate be used again. The salts analyzed in this study, provided by Sigma Aldrich (St. Louis, MO, USA), were barium chloride (BaCl₂), strontium nitrate (Sr(NO₃)₂), Lithium sulfide (Li₂S), rubidium chloride (RbCl). The salts were dissolved in de-ionized water in a parent stock from which solutions with concentrations: 1, 3, 5, 10, 15, 25, 50, 75, and 100 ppm were prepared.

2.2. LIBS analysis
LIBS Spectra were acquired over the spectral range from (200 nm) to (1100 nm). The intensity of the laser was kept constant over all measurements. We chose the intensity such that clean spectra were acquired in each case without much background and typically with a large signal-to-noise ratio for the most intense peaks in each spectrum. Saturation was avoided at this setting as well. The energy per pulse depends on the analyzed salt and was between 65.5 and 85.5 mJ per pulse, according to the settings of the laser fabricant. The laser spot was focused about two mm below the surface to avoid damage to the support material. This was monitored with the instrument’s inbuilt camera inspection system. A spectrum is showed in figure 2 of strontium nitrate (10 ppm) deposited on steel surface scratched with a HB pencil.
In most cases the pencil substrate had a sensitivity comparable to that of the graphite plates and higher than the other substrates as measured by peak height. In figure 3 we show this for one peak of strontium (640.8 nm, 75 ppm). Overall, the graphite plates and the steel surfaces scratched with a HB pencil showed better linearity and sensitivity than the other substrates.

Figure 2. \(\text{Sr(NO}_3\text{)}_2\) spectrum (10 ppm) on the HB pencil substrate, with some \(\text{Sr}\) peaks highlighted.

Figure 3. Different substrates for \(\text{Sr}\) (640.8 nm, 75 ppm), steel surface scratched with a HB pencil, and graphite plates were the best behavior.
2.3. Data collection

We collected 5 spectra for each concentration in all cases. The number of spectra depends on the target spot because the liquid substance (1 µl) does not dry uniformly. Both single shot and five-shot averaged spectra were registered and studied. In each case, the shots were made in different places on the dried spot. The measurements were made three times to check for reproducibility and to improve statistics. The spectra that remained after this elimination were averaged in each case.

The data we discuss here are the averages of these data sets for LiSO$_4$, RbCl and BaCl$_2$, and 3 spectra for Sr(NO$_3$)$_2$.

We chose the peaks indicated in table 1 to monitor lithium, strontium, barium, and rubidium in their respective salts. These peaks were always clearly identifiable and measurable as they had a good SN ratio.

| Table 1. Wavelengths in nm of the spectral peaks used to characterize the cationic components of the salts investigated. |
|---------------------------------------------------------------|
|                  | LiSO$_4$ (Li) | Sr(NO$_3$)$_2$ (Sr) | BaCl$_2$ (Ba) | RbCl (Rb) |
| Peak 1           | 610.365       | 460.733             | 553.548       | 420.883    |
| Peak 2           | 670.79        | 640.847             | 652.731       | 780.027    |
| Peak 3           | 812.78        | 650.4               | 659.533       | 794.76     |
| Peak 4           | 707.01        | 705.994             | 794.76        |            |
| Peak 5           | 728.03        |                     |               |            |

2.4. Data Analysis

Peak areas were calculated with the numerical tools provided by the software of the data acquisition system. According to the manufacturer, a peak is defined by a centroid and two wing wavelengths. At the same time, these wing values define the local background and baseline for the peak. The area below the curve between the wings values and above the baseline is defined as the peak area. Spectral lines corresponding to measured peaks are determined by comparison of the centroid under a given wavelength tolerance, on a spectral library.

For establishing calibration curves, we have compared the cases in which the calibration curves were made out of raw data for which no special consideration was made on the absolute value of the peak areas for given concentrations with other curves where outliers have been removed to improve linearity and minimize error.

3. Results and Discussion

3.1. Outliers treatment

Most peaks in every spectrum collected for a given concentration fell reasonably close to the mean value, showing positive and negative deviations from this value. This fact allowed us to calculate mean values with low relative dispersion. However, in some cases, as is common in LIBS, either extremely intense or low peaks can be recorded for the same element under the same experimental conditions [24]. With regard to our data, this extreme-value peaks introduce a large bias because few spectra are average introduce contributing to a large standard deviation and margin error.

In our case, as a simple non-supervised quantitative tool to select outliers, we proceeded as follows. First we calculate the average value of the areas of each peak at the measured concentration. Second, we compared each value with the next higher and lower concentration. If a peak was found to be higher or
lower than those mean values, respectively, it was considered an outlier and removed from the data set. Definitive average values for each concentration were determined from this reduced data set. In figure 4, a concentration calibration curve for lithium before described outlier treatment is shown. Large standard deviation values (error bars) are visible even if linearity is not too low. In figure 5, the same curve is shown for this peak after outlier treatment was applied, showing clear improvement in linearity and error reduction.

The graphite plates and steel surfaces scratched with a HB pencil yielded the best results (linearity and sensitivity) in our substrate comparison analysis. These types of substrates have been previously validated with LIBS and MALDI techniques [20-22, 25].

In figures 5 and 6, we show other calibration curves calculated as described, also showing good analytical performance.

**Figure 4.** Calibration curve for peak 3 of Li. Correlation coefficient R= 0.85024. Errors and standard deviations are relatively large.

**Figure 5.** Calibration curve for peak 3 (812.78 nm) of Li. Correlation coefficient R= 0.97181. The improvement in analytical performance as compared to figure 4 is clear.

**Figure 6.** Calibration curve for peak 1 of Rb obtained with the outlier treatment described in the text. R=0.9611.
The benefits of the aforementioned outlier treatment can be demonstrated by the fact that the correlation coefficients without treatment were in the range from 0.75 to 0.95 for all elements and were accompanied by high error bars in the calibration curve. After the outlier treatment was applied to the datasets correlation coefficients improved substantially to be within 0.90 a 0.98, and the error was much less (as the error bars in figure. 5 and 6 illustrate). Results for all samples and peaks are summarized in Table 2.

We believe that the physical basis underlying the outlier treatment described can be explained by the fact that, despite the good surface characteristics of the substrate used, the generated crystals are of variable sizes and, consequently, subject to random distribution on the spot. In this way, each laser shot hit on a fresh spot, finding slightly different salt crystal coverage, and should consequently produce even under the same irradiance conditions, different amounts of light emitting atoms. Thus, if relatively big crystals are hit, then more intense peaks should be produced. By the same token, relatively poorly covered areas should produce less intense signals.

Ideally, the calibration curves should cut the Y (Area) axes at 0, however in these calibration curves, it is not the case. We attribute this to an unwanted background on the basis LIBS signal. We are studying ways to improve this.

Additionally, since we registered peaks with good signal-to-noise ratio for all peaks we included in the analysis, we can safely say the detection limit for all these substances with this method is below 1 ppm on all cases.

Table 2. Parameters of calibration linear fittings for the peaks corresponding to each salt. The slope, intercept, and correlation indices, for each curve are reported.

|       | LiSO₄ (Li) | Error | Sr(NO₃)₂ (Sr) | Error | BaCl₂ (Ba) | Error | RbCl (Rb) | Error |
|-------|-----------|-------|--------------|-------|------------|-------|-----------|-------|
| Peak1 | 610.365   | 460.733| 553.548      | 420.883|            |       |           |       |
|       | 193.5     | 23.03  | 383.7        | 143.5 | 630.9      | 90.9  | 43.0      | 12.8  |
|       | 9.5       | 0.49   | 20.2         | 2.76  | 29.2       | 2.2   | 3.9       | 0.2   |
|       | 0.978     | 0.897  | 0.961        |       | 0.961      |       |           |       |
| Peak2 | 750.05    | 45.4   | 51.9         | 159.6 | 68.2       | 157.2 | 33.0      |       |
|       | 13.3      | 1.2    | 12.1         | 1.0   | 12.9       | 1.6   | 7.9       | 0.71  |
|       | 0.937     | 0.960  | 0.894        |       | 0.938      |       |           |       |
| Peak3 | 812.78    | 650.4  | 134.3        | 58.1  | 49.6       | 18.3  |           |       |
|       | 20.7      | 11.0   | 36.2         | 42.2  | 10.9       | 1.4   | 4.6       | 0.3   |
|       | 3.9       | 0.2    | 9.3          | 0.8   | 0.956      | 0.892 |           | 0.944 |
|       | 0.971     | 0.956  | 0.892        |       | 0.944      |       |           |       |
| Peak4 | 707.01    | 705.994| 99.6         | 36.4  |            |       |           |       |
|       | 23.9      | 29.5   | 7.8          | 0.8   |            |       |           |       |
|       | 6.0       | 0.5    | 0.917        |       |            |       |           |       |
|       | 0.949     | 0.917  |             |       |            |       |           |       |
| Peak5 | 728.03    | 71.5   | 22.1         | 4.4   | 0.5        | 0.917 |           |       |
|       |           |        |              |       |            |       |           |       |
The figures presented here demonstrate the very good analytical response of the sample preparation and data analysis methods, but specially that of the newly introduced substrate. In terms of analytical performance, it is possible to determine peak sensitivity (as measured by the slope) from the data presented in Table 1. This can then be used to monitor corresponding cation concentrations. The measurement of one or more peaks for practical application would depend on the situation or needs of the study. In this way, we have introduced a simple and inexpensive substrate with very good performance in the analysis of salts dissolved in water by the dried–droplet method.

4. Conclusions
In this paper we have introduced a new substrate for the quantitative analysis of salts dissolved in liquids with Laser-induced Breakdown Spectroscopy (LIBS) consisting of a steel surface scratched with a HB pencil lead. The analytical capabilities of this system are demonstrated by the analysis of the crystalline deposits formed by the dried aqueous salt solutions. We achieved very good sensitivity and linearity (correlation coefficients in the order of 0.9-0.98) for each ion analyzed. These results were consistent over a set of four salts ($\text{Sr(NO}_3\text{)}_2$, $\text{LiSO}_4$, $\text{RbCl}$, and $\text{BaCl}_2$) for concentrations between 1 to 100 ppm. For quantification, the areas of specific peaks for each cation were used as a measure of the concentration of the salt.

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