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Processing of shot-to-shot raw data to improve precision in laser-induced breakdown spectrometry microprobe ☆

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ABSTRACT

In order to set up the precision limit that can be reached with laser-induced breakdown spectrometry microprobe, a steel sample was scanned by using a 6-μm diameter spot. Besides being close to the limit of the technique, such a spot diameter resulted in a small plasma size that minimized self-absorption effects. To minimize shot noise, Cr and Fe were used as test elements because of their high contents. Scan consisted of 25 successive matrices formed by 5×6 shots, i.e. a total of 750 shots. Results were studied as a whole, as well as between matrices and within matrices, to search for inhomogeneity, outliers and drift. Except a few outliers, the main contribution in the experimental RSD was the drift either within a matrix or between matrices. Drift attributed to laser warm up could be compensated for either by using a polynomial fitting or by using the other element. %RSD significantly below 2 were then obtained demonstrating that there is no penalty in terms of precision to perform laser microprobe using a series of single shots.

1. Introduction

Laser-induced breakdown spectroscopy is fully appropriate to provide determination of roughly all elements in all types of environment, and in a large variety of matrices in the solid, liquid or gaseous phases. Since the introduction of LIBS by Debras-Guedon and Liodec in 1963 [1], significant work has been performed that demonstrate the high potential of LIBS in many different fields. Several instruments have been made commercially available in the early 1970s [2,3], but they never gained a total acceptance. A major reason was a lack of sufficient reliability of lasers and spectroscopic detection system available at that time to provide analytical results with an acceptable level of accuracy.

The interest for LIBS was recently renewed by progress in instrumentation that led to the development of new compact, sometimes portable, lasers and spectrometers, fully adapted to in-situ multielemental analysis. Besides, interest of LIBS is not questionable for new fields of application such as stand-off analysis for security, environment, planetary exploration, among others, along with microanalysis for fast elemental mapping of surfaces.

From a fundamental point of view, the understanding of phenomena involved in laser–surface interaction, benefits from the large research efforts performed in other fields of analytical application like laser ablation-ICP MS [4], or in laser-material processing like thin film laser plasma deposition [5].

Regardless of the field of application, acceptability of LIBS is still related to the problem of quantitation, involving accuracy, i.e. repeatability and trueness. The level of accuracy depends on the analytical problem, but there should be a balance between repeatability and trueness. One of the emerging applications is laser microanalysis, which was possible thanks to the focusing properties of the laser beam. Laser microanalysis should be relevant to any spot diameter below the bulk homogeneity of the sample. Taking into account the homogeneity scale of most materials and competitive techniques, a lateral resolution below 10 μm is required [6–10]. This technique may be called microLIBS, although LIBS microprobe would be more appropriate. The probed material volume is usually very small, particularly when combining a single shot with a diameter below 10 μm, leading to an amount of ablated material of the order of ng. Repeatability may be of concern with LIBS microprobe. In this case, the amount of photons emitted by the microplasma can be very small, and sources of noise dependent upon the number of photons, shot noise and detector noise, may be significant or even limiting.

The purpose of this work was to study the nature of the shot-to-shot noise and its possible compensation for when performing LIBS microprobe. A steel sample was selected for this study by using Cr and Fe as test elements.

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2. Experimental

The instrument has been previously described [6]. A Nd:YAG Minilite-1 laser (Continuum, USA) was operated at 10 Hz with an output energy of 3 mJ at 266 nm and a 4 ns pulse duration. The laser beam passed through a filter, resulting in a top-hat irradiance of 50 GW cm^{-2} at the sample surface. The same 25× microscope objective (Ealing reflective objective with a numerical aperture of 0.4, working distance 14.5 mm, coated for 266 nm laser light, Ealing Electro-Optics, Warlord, UK) was used both to focus the laser beam onto the sample and to collect the light emitted from the plasma. The resulting spot diameter was 6 µm so as to be near the limit of the laser microprobe technique [9]. The sample is positioned on a high precision motorized XY translation stage (MCL-2, Märzhäuser, Germany, 0.1 µm precision). The stage is computer driven so that it is stopped each time a laser shot should be synchronously fired on a fresh surface, and is then moved between two successive shots. In this work, the surface of the sample was scanned using 25 matrices consisting of 5×6 shots, i.e. a total of 750 shots. The *x*–*y* distance between shots was 25 µm within a matrix. When using laser microprobe in chemical mapping mode, the distance between shots is usually the same as the laser spot diameter, but a 25-µm space was selected to avoid any possible influence of reablation of the edge of a crater on precision. The target was automatically displaced during a matrix acquisition, whereas a manual repositioning was used to move to the location of the first shot of the next matrix. It was followed by a refocusing of the beam by means of a He–Ne laser, the spot of which is measured at the surface level through a camera. Time for a matrix scan was, then, 3 s, and a total time to scan the target was less than 20 min.

The spectrometer (DILOR SA, Lille, France) consists of a 0.5-m focal length dispersive system, a 3600 line mm^{-1} grating, and a gated intensified photodiode array (Reticon, USA, 700 intensified photodiodes). The 700 photodiodes led to a spectral window of 7 nm in the visible region, with a bandpass of 10 pm $pixel^{-1}$. The intensity was measured by integration over 5 pixels corresponding to the experimental line FWHMs.

The steel sample was selected for its large Cr concentration (26.72% Cr and 36.71% Fe) so as to minimize the shot noise, as justified below. Two Cr and two Fe lines were selected because they could be simultaneously measured within the same 7-nm spectral window of the spectrometer, 422–429 nm. A pair of lines was selected for each element for shot-noise evaluation, as laser-related fluctuations should be similar for both lines. Besides, the Fe or the Cr excitation energies are very close together so that they should behave similarly to any change in the plasma temperature. Their wavelengths and excitation energies are given in Table 1. Because the Cr lines are resonant, they could suffer from a significant self-absorption. However, one feature of a 6-µm laser microprobe was to produce a very small microplasma, thus minimizing the self-absorption effect.

3. Results

It should be noted that precision is a broad term that includes both repeatability and reproducibility. Clearly, repeatability is related to shot-to-shot variability within a given matrix. Reproducibility implies that at least one parameter has been changed in purpose, usually to study its influence. However, between matrices, some changes may occur such as homogeneity and flatness of the sample, or drift of the laser energy resulting in a change in plasma characteristics. Strictly speaking, this variability is not a reproducibility as no parameter has been intentionally changed, except the position on the sample. The concept of intermediate precision could be more appropriate.

Table 1
Wavelength (nm) and energy (cm^{-1}) of the Fe and Cr lines

Line	Wavelength	Upper level	Lower level
Fe I	430.8	35,765	12,561
Fe I	427.2	35,379	11,976
Cr I	429.0	23,305	0
Cr I	427.6	23,386	0

3.1. Origin of the noise

Major sources of noise in LIBS measurements may have four different origins: (i) noise due to laser-related plasma fluctuations such as shot-to-shot laser energy, rate of ablation, and plasma characteristics (mainly atomization yield and excitation temperature), called source noise; (ii) shot noise due to the random arrival of the photons on the detector; (iii) detector noise; and (iv) drift. The source noise is usually a flicker noise, i.e. its standard deviation is proportional to the signal. In other words, its relative standard deviation, RSD, is constant. Shot noise follows a Poisson statistics, i.e. the standard deviation is proportional to the square root of the number of photons arriving on the detector during the exposure time. If the detector noise is neglected, the %RSD can be written:

$$\%RSD = 100\left[\alpha^2 + \frac{\beta}{z\cdot\tau} + \delta^2\right]^{1/2} \quad (1)$$

where α is the flicker noise coefficient, z is the signal intensity in electron $pixel^{-1}$ s^{-1}, τ is the exposure time, β is a shot-noise coefficient, and δ is the contribution of a possible drift. Because of short exposure times inherent to pulse-based plasma, the only way of minimizing photon noise is to have a high signal intensity. Besides decreasing the resulting %RSD, the remaining sources of noise may be time-correlated, in contrast to shot noise-limited signals, which are inherently non-time-correlated. Time-correlation makes it possible to improve precision by using internal standardization.

To estimate the signal intensity for which shot noise would be considered negligible, samples with a large range of Mn concentrations were used to provide an intensity variation in the range 50–15 000, using similar acquisition conditions. Experimental data are given in Fig. 1. Using Eq. (1), the best fitting was obtained for $\alpha^2+\delta^2 = 0.08^2$ (i.e. a %RSD of 8) and $\beta = 18$ (Fig. 1). In other words, a shot-noise free signal would exhibit a value in the range 6–10 % RSD. From Fig. 1, it may be seen that intensities higher than 20 000 are required to minimize shot noise. With the selected Fe–Cr sample, intensities were in the range 40 000–60 000 for the Fe and Cr lines. At this level, the contribution of the shot noise would be near 2% with $\beta = 18$. Because, the measured %RSD of the laser shot-to-shot noise was only 4% after warm up, there was at least another important cause of noise, i.e. drift, without forgetting the possibility of either outliers, or sample inhomogeneity. Raw data will be then examined to explain the experimental %RSDs.

3.2. Measurements

The 750 shots were considered as a whole. In this case, the %RDS was 6.0 for Cr 427.6 nm, 6.8 for Cr 429.0 nm, 7.3 for Fe 427.2 nm, and 7.5 for Fe 430.8 nm, i.e. an average of 6.9, which was in the range deduced from the Mn experiment. The %RSD using the Cr 427.6 nm/Cr 429.0 nm and Fe 427.2 nm/Fe 430.8 nm line ratio, was 3.8 and 3.95, respectively, corresponding to a contribution of the shot noise near 2.8%, i.e. not too far from the Mn extrapolated value, 2%. Once again, another source of noise must be identified, with a preliminary search for possible outliers.

3.2.1. Search for outliers

Outlier search was performed by using the Hampel test or score [11]. One advantage of this test is to avoid any assumption on potential