Corrections for variable plasma parameters in laser induced breakdown spectroscopy: Application on archeological samples☆

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ABSTRACT

The final scope of this work was to determine the elemental composition of different types of decorative layers present on ancient ceramic fragments through depth profiling by laser induced breakdown spectroscopy (LIBS). The measurements were performed by a stand-off LIBS system at distance of 10.5 m, by employing ns laser pulses at 1064 nm and an Echelle spectrometer. The detected plume intensity strongly differs from one sample/coating to another and changes importantly also in repeated measurements on the almost homogeneous bulk materials. Furthermore, the plasma intensity and its parameters widely change during the depth profiling, as evident from the ratio of here monitored Fe I and Fe II spectral lines. Averaging the line intensities over six repeated measurements, also on the bulk material and for a selected consecutive shot number, produces the errors up to 60% around the mean value and this makes impossible to compare composition of the ceramic body with its decorative layers. To overcome this problem, we developed a theoretically supported procedure for the spectral line corrections in presence of variable plasma parameters, which considers the relative changes among a sufficiently large data set. This method allowed improving the measurement precision up to five times, obtaining a flat response during the depth profiling, and measuring composition of the surface layers. The correction factors are specific for one analytical line of the considered element. The proposed procedure could be universally applied for increasing the LIBS precision in repeated samplings or during the depth profiling, without time consuming calculations of the plasma temperature and the electron density, which also suffer from large measurement errors.

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1. Introduction

Among different atomic spectroscopy techniques [1], in the last two decades laser induced breakdown spectroscopy (LIBS) evolved rapidly [2–3], helped by a development of the commercial laser sources and the broad range spectrometers. LIBS became one of the most promising techniques for ultra-rapid, in-situ identification of materials [2–5] as it does not require any sample preparation. Individual sampling can be carried also at KHz rates [6], important for detection of moving objects. LIBS measurements are contactless and feasible at distances up to 130 m [7–8]. The theory and the updated state of art relative to different LIBS applications, including analysis of metals, geological materials, aerosols, liquids, biological samples and many others, are collected in [9].

LIBS is based on plasma generation by an intense short laser pulse, which leads to atomization and ionization of the sample material.

Spectral emission from the excited species in plasma, which temperature might exceed 10,000 K, is used for qualitative identification and eventual quantification of the sample composition. Methodologies for obtaining semi-quantitative or quantitative sample analysis by LIBS are reviewed in [10]. Retrieval of the element concentrations from the LIBS spectra is usually based on an initial univariate or multivariate calibration by the matrix matched certified samples [11–14] as the line intensities in the plasma strongly depend on physical and chemical properties of a material. Quantitative LIBS measurements are difficult to achieve on unknown materials, as often happens with geological samples [13,15]. For example, the ChemCam instrument for Mars exploration was calibrated by using 69 different rock types and in some cases, the LIBS measured contents even of some major elements (like silica and iron), differs the up to 30% from the true values [13].

Another approach for retrieval of the element concentrations in the sample is so called calibration free (CF) method, recently reviewed in [16]. This method is based on assumptions of: a) stoichiometry between the element contents in the sample and their atomic/ionic densities in the plasma; b) local thermal equilibrium (LTE) in the plasma [17] during the signal acquisition; c) existence of a homogeneous optically thin

plasma; d) all major and most of the minor elements in the sample are detected in the LIBS spectra, and this requires to use a broadband spectrometer (an Echelle or a spectrometer array). The broadband spectra, corrected for the instrument response, are then processed to calculate the plasma temperature and its electron density, and to derive afterwards the element abundances basing on Boltzmann-Saha equations. The CF approach produces good quantitative results only on very simple matrices like binary alloys while in other cases a reasonable accuracy is achieved only for major sample elements [16,18].

Archeological objects exhibit a great variety of materials with very different physical and chemical properties, among them: bronzes, precious alloys, marbles, glasses, ceramics, pigments and many others. These materials often have the unique characteristics, very difficult to reproduce i.e. to create the matrix matched samples for calibration. However, even in absence of the quantitative results, LIBS became one of leading analytical techniques in the area of cultural heritage [8,19–21] thanks to its capability to perform element mapping and stratigraphy in-situ [22–24].

When analyzing an ancient pottery and its decorative layers as in the present work, usually the matrix is unknown and its complexity is analogue to that of geological samples [25]. Typical relative standard deviation (RSD) of the LIBS line intensities mapped on soils and rocks is between 10 and 30% [26–28], where the uncertainty further increases for low intensity analytical lines [29]. During the depth profiling of geological samples the data scattering might be even larger: in [30] the measured intensity of different atomic Ca lines during the crater drilling at the laser repetition rate of only 1 Hz, was between 35% and 90%, increasing with a number of the delivered laser shots. In fixed experimental conditions, shot-to-shot LIBS signal fluctuations [29,31] may arise from: the laser source instability, not constant coupling between laser-sample and laser-plasma, variable ablation and plasma excitation rates, dependent on the sample's chemical and physical properties (e.g. absorption of the laser, roughness, grain size and melting/vaporization temperature), then the aerosol's persistence after the previous laser shots, moisture in the sample and in the surrounding atmosphere. A significant improvement in the LIBS signal stability might be achieved by normalizing it by the continuum plasma emission, the integrated plasma intensity or by a line intensity from some major element in the sample [12,32]. Even in well controlled experimental conditions and sampling a very homogeneous flat glass, the line intensity ratios of two elements might exhibit large shot-to shot fluctuations (c.a. ±20%), here attributed to a variable non-stoichiometric ablation [33]. By calculating the plasma temperature and its electron density after each laser shot, and by correcting the line intensities according to Saha-Boltzmann equations [33,34], the signal fluctuations were reduced for about factor 3; the correlations factor of the calibration curves based on the element ratios, significantly improved after the data correction [33]. However, this approach suffers from the time consuming calculations of the plasma parameters for each spectrum acquired, which introduce additional, large errors. Also, if not using a wide range spectrometer, the detected lines might be insufficient for calculation of the plasma parameters.

Recently, an attempt to correct empirically the LIBS measured line intensity ratios of two elements for the plasma temperature variations without calculating the same, has been reported in [27]. The samples considered were different types of powdered rocks and certified soils, thus a large data scattering due to the matrix effect might be expected. The proposed data elaboration procedure, based on retrieval of four fitting coefficients from the acquired data set, was called Optimize Calibration (OC) and it allows for fast, in-situ data elaboration. With respect to the traditional calibration, OC improved the linear correlation between the measured line intensity ratios and the certified element ratios in samples, but the final prediction errors still remains large, between 9.5% and 33%.

In this work, we developed a procedure for the empirical corrections of the line intensities due to variable plasma temperature and its electron density. This procedure reduces RSD in repeated measurements and in depth profiling by LIBS. The model was developed starting from our previous work [34] where the correction coefficients had been derived both for atomic and ionic analytical lines. The line intensity corrections, together with a normalization due to variable ablation rate on different materials, was exploited to determine composition of the decorative layers with respect to the bulk ceramic material. So obtained results are compared to the sample characterizations by other analytical techniques.

2. Experimental

The LIBS system (Fig. 1) is a home built laboratory prototype for stand-off measurements at distances between 8 and 30 m. It incorporates a Quantel Q-Smart laser emitting 6 ns pulses at 1064 nm with the available energy of 850 mJ at repetition rates up to 10 Hz. The energy stability guaranteed at 1064 nm is ±2%, while the pointing stability is better than 40 μrad. The beam is guided by a five mirror articulated arm to a beam expanding/focusing system containing one negative lens, mounted on a motorized slit, and two positive lenses of diameter 50 mm. The lens system (LS) is fixed on a precisely rotating table, necessary to make coincide the laser focal spot with the telescope axis at different target distances. The working distance is measured by a laser range finder (LRF), DIMETIX Mod. FLS-C10. The red beam from the LRF (630–690 nm) is introduced into the path of the high power laser through the last (dielectric coated) mirror of the articulated arm.

The plasma emission is collected by a Galilean telescope, whose primary mirror (M1) has diameter of 350 mm and focal length of 1600 mm; the secondary mirror (M2) is an elliptical flat. Both mirrors have AlMgF coating, highly reflective from UV to NIR. The primary mirror is mounted on a motorized slit, used to adjust the focusing according to the measured target distance.

At the telescope exit, a quartz plate is placed to reflect partially the sample image onto a CMOS color camera. The LIBS signal, after passing a meniscus quartz lens (f = −200 mm), is collected by a quartz fiber (800 μm) and brought to an Echelle spectrometer (ANDOR, Mechelle 5000); the corresponding spectral resolution is between 0.18 nm at 250 nm and 0.45 nm at 770 nm. The spectra are registered by an ICCD detector (ANDOR DH334T) triggered by the properly delayed laser's Q-Switch output.

All the measurements were conducted at the target distance of 10.5 m and with the laser pulse energy of 450 mJ. The laser spot diameter on the sample was 1.3 mm, corresponding to the flence of 34 J/cm^2. The LIBS spectra were registered at delay of 3.5 μs from the laser pulse, necessary to avoid the detector saturation; the acquisition gate was set to 10 μs. To minimize the breakdown occurrence on aerosol generated by the previous laser shots, the laser repetition rate was limited to 1 Hz. The samples were mounted on a motorized X–Y table for selecting precisely, with help of the camera, areas to probe by the laser (Fig. 2-left).

We performed the measurements on about forty different ceramic fragments extracted from the archeological site Teotihuacan (Mexico) and belonging to period 150 b.C–350 a.C. Here, we discuss only one sample – Patlachique 7, a jar fragment dated 150 b.C–1 a.C. This item is particularly interesting because covered by a glaze (brown), overpainted with red and white pigments. All three types of the surfaces were sampled at six points (Fig. 2-right) by applying twenty consecutive laser pulses, after each the spectrum was registered separately. The analogue sampling was carried out on a freshly broken ceramic body i.e. bulk material, where the surface was visibly rough.

Volume of the craters after twenty laser pulses was measured by a confocal microscope Olympus FV 1000, with the excitation light at 473 nm. Images of the samples were acquired in the spectral range 485–545 nm with lateral and depth resolution of 1.6 μm and 1.0 μm, respectively. Comparative chemical analysis as performed by: