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THE ANALYTICAL CAPABILITY OF LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS) BASED ON TEA CO₂ LASER SYSTEM

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ABSTRACT

This paper gives an overview of analytical capabilities of the laser induced breakdown spectroscopy (LIBS) system, based on Transversely-Excited Atmospheric pressure (TEA) CO₂ laser, and time-integrated, spatially-resolved detection, for the analysis of solid materials. The developed LIBS system is unique, and differs from the commonly used systems in two respects. The first one is the laser used as an energy source for plasma generation, and the second one is the applied non-gated detection scheme. Various types of materials were analyzed, from metals to biological samples, under different experimental conditions. The obtained results were critically evaluated and compared to the results obtained using commercially available LIBS that comprises Nd:YAG laser and time-gated detection. It was concluded that when it comes to detectability, precision and sensitivity, this simple and cost effective LIBS system may be regarded highly competitive to standard LIBS systems.

INTRODUCTION

LIBS is a contemporary optical emission spectroscopy method that uses the optical signal from laser-generated plasma to study elemental composition of a sample. In this technique, laser radiation interacts with the material causing its ablation, vaporization, ionization and, at sufficiently high power densities, creation of plasma of the irradiated material. In plasma, the species are excited to emit element specific radiation which is analyzed by the spectrometer. Using the information provided by emission spectra, both qualitative and quantitative analysis could be performed. In a review article by Hahn and Omenetto [1], unique features of LIBS were summarized in one sentence: "Suffice it to say that LIBS, in principle, can directly address and simultaneously detect all neutral and ion spectral features of all atomic

and molecular species of all elements present in any type of sample and its surrounding environment using a single laser shot". In 2004, LIBS was promoted as the future superstar of atomic spectrometric methods [2], and twelve years later we may see that LIBS has been successfully applied in a variety of fields ranging from cultural heritage to space explorations [3].

Contrary to qualitative, quantitative LIBS analysis is not an easy task and has been considered the "Achilles heel" of the technique [4]. One of the main difficulties for a precise and accurate quantitative analysis by LIBS is due to matrix effects, to which laser induced plasmas can be very sensitive. For quantitative analysis of solids, the sample matrix must closely match the matrix of the standards, and appropriate standards are often difficult to obtain. Thus, further improvements of LIBS technique require new instrumental and analytical approaches in order to overcome problems connected with matrix effects and calibration issues, as well as research aimed at lowering the limit of detection, and improved precision and accuracy of measurements.

CHARACTERISTICS OF LIBS SYSTEM BASED ON TEA CO₂ LASER

Analytical performance of LIBS depends on many experimental parameters, the most important being laser characteristics (power, wavelength, pulse length, beam profile), ambient gas and its pressure, geometric setup and time of observation. As a consequence, optimization of experimental conditions is needed for each particular application. Although different experimental configurations are reported in the literature, a nanosecond Q-switched solid-state Nd:YAG laser is most often for LIBS [5]. Thus, a "conventional" LIBS comprises of three basic components, Nd:YAG laser, a monochromator coupled with an Intensified Charge Coupled Device (ICCD) and a pulse generator to synchronize the plasma production and the emission spectra acquisition. In that sense, TEA-CO₂ LIBS system may be regarded as "unconventional" because of the laser used for plasma generation, and also because time-integrated spatially resolved detection was used for acquisition of emission spectra.

Laser characteristics

The laser source for LIBS was a commercial version of the TEA CO₂ laser system developed at the VINCA Institute of Nuclear Sciences. Pulsed TEA CO₂ laser emits radiation at 10.6 μm , with an output peak power typically in the order of megawatts. The laser-optical pulse has a gain-switched spike, followed by a slowly decaying tail. The full width at half-maximum

(FWHM) of the spike is about 100 ns, and the tail about 2 μs , Fig. 1. About 35% of the total irradiated laser energy is consisted in the initial spike.

Compared to the most commonly used solid state laser Nd:YAG, TEA CO₂ laser has lower photon energy and longer pulse duration (~ 0.12 eV, 100 ns for TEA CO₂ compared to ~ 1.17 eV, 10 ns for Nd:YAG). As a consequence, differences regarding the ablation process, plasma parameters and plasma expansion dynamics are to be expected. The advantage of Nd:YAG laser compared to CO₂ laser is higher mass ablation rate per pulse [6]. However, longer wavelength of CO₂ laser, and specific temporal profile of the pulse (ns peak followed by μs tail), may produce a plume with better properties for analytical applications [7,8].

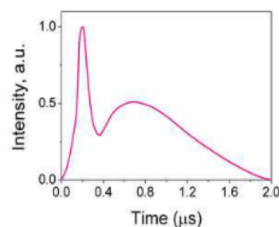


Figure 1. Temporal profile of TEA CO₂ laser pulse.

Detection scheme

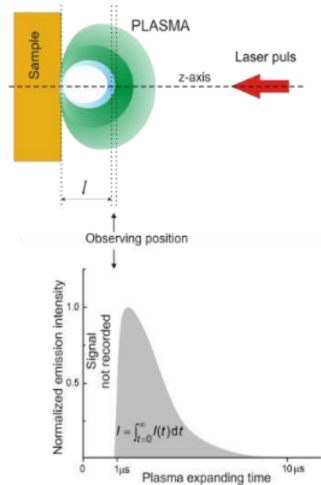


Figure 2. Schematic representation of time-integrated, spatially-resolved detection of plasma emission.

Laser-induced plasma is transient in nature, i.e., characteristic plasma parameters (like emission intensity, electron number density, electron temperature, etc.) evolve in space and time. In LIBS applications, a key objective is to reduce the spectral continuum background intensity compared to the discrete line signal intensity. Usually, to achieve this goal, temporal gating of the emission signal is used, which utilizes the fact that different decay rates characterize the continuum emission and atomic emission processes. Therefore, temporal resolution is used for optimizing the signal-to-noise and signal-to-background ratio, which are a function of delay and integration times.

In our LIBS system temporal resolution was replaced with spatial resolution, Fig.2. Obviously, the two approaches are correlated, because the plasma reaches a given distance above the analyzed surface with a certain time delay. A time-integrated space-resolved laser induced plasma spectroscopy (TISR-LIPS)

utilizes the fact that intense continuum emission is mostly emitted from a region close to the sample surface, while in further-out regions of the plasma the continuum emission is largely reduced [9]. The obvious advantage of this method is reduced complexity of the detection system and its cost (eliminating the need for expensive time-gated detectors). Characteristics of TEA CO₂ laser pulse (wavelength and pulse duration) are favorable for non-gated detection of spectral lines. The leading edge of the CO₂ laser pulse creates plasma, while the remaining part of the pulse (tail) interacts with the plume through the *inverse Bremsstrahlung*, IB. The rate of IB absorption (α_{IB}) is strongly dependent on laser wavelength λ ($\alpha_{IB} \sim \lambda^3$), which means that laser-plasma interaction is much stronger in the case of CO₂ laser than the Nd:YAG laser [10]. Efficient IB absorption reheats the plasma. Long wavelengths are efficiently absorbed by the plume causing an additional plasma excitation and expansion, which increase the LIBS signal through enhancement of emission lines. Consequently, in low density regions far from the target surface, spatial discrimination between line and continuum emission is improved, and line broadening reduced. In addition, the dimensions and lifetime of plasma increase with pulse duration. The plasma takes longer to decay and hence, the emission lasts longer.

ELEMENTAL ANALYSIS OF SOLIDS BY TISR-LIPS BASED ON TEA CO₂ LASER

Analytical capability of the plasma induced by IR TEA CO₂ laser pulses was evaluated for three different types of solids, metals and alloys, geochemical, and biological material.

Metals and alloys

TEA CO₂ laser based LIBS was applied for elemental analysis of metals and alloys (Cu, brass, bronze, Ti, Al alloys) [9,11-13]. Due to high reflectivity of the metals in mid-IR region, generation of metal target plasma, with low intensities of TEA CO₂ laser pulses was relatively difficult to obtain. Most metals have high melting, as well as normal boiling temperature, thus heating of the metal surface by IR laser pulse was the most critical stage for plasma generation. In the case of copper, the situation was even more complicated, because copper has high diffusivity and thermal

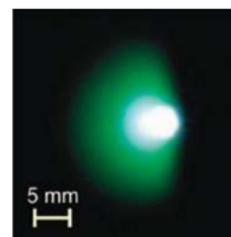


Figure 3. Cu plasma produced by focused CO₂ laser beam at air pressure of 0.1 mbar.

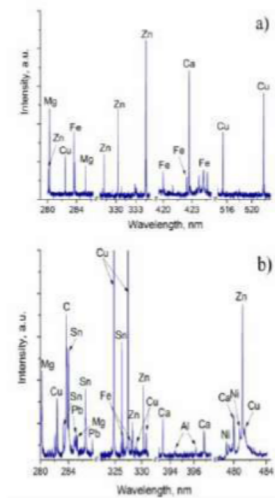


Figure 4. LIBS spectra of (a) brass and (b) bronze

optimum air pressure for target plasma formation was 0.1 mbar.

In Fig. 3, image of the Cu-plasma produced by focused CO₂ laser beam (laser fluence 8.6 J cm⁻², intensity 30 MW cm⁻²) is shown. The plasma had a semi-spherical shape with two clearly visible, spatially separated regions usually denoted as primary and secondary plasma).

For all investigated metal samples, spectra consisted of sharp spectral lines (Fig. 4) and relatively large signal to background and signal to noise ratios were obtained. For Cu and Cu based alloys, estimated limits of detection (LODs) of trace element were in the range of 10 ppm, i.e. of the same order as obtained with standard LIBS. In addition, TEA CO₂ laser radiation induced negligible damage on the investigated samples, which is important if this LIBS system is to be applied for the analysis of cultural heritage objects.

Another example is quantitative

conductivity, so the heat deposited on the surface spreads rapidly into the bulk. At high pressures, plasma generated by ns-pulse was always accompanied by simultaneous formation of the gas breakdown plasma. However, the threshold for plasma formation was significantly reduced by increasing the target absorptivity (by increasing the surface roughness) and reducing the pressure. Lowering of the air pressure reduces the extent of gas breakdown, enabling better laser-target coupling because of a less plasma shielding. Better heating of the copper surface by IR laser pulse was achieved, and thus ablation was increased. Below 10 mbar, the spectrum consisted only of copper emission lines, which means that the plasma was ignited in a vapor without initiation of a gas breakdown. The

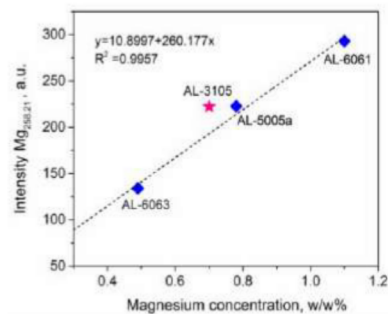


Figure 5. Calibration curve for Mg in Al-alloys.

analysis of metal samples. TISR-LIPS based on TEA CO₂ laser was applied to determination of Mg in Al-alloys under reduced air pressure. A calibration curve for Mg was constructed using certified aluminium alloy samples Fig. 5. A linear relationship between LIBS signal and analyte concentration was obtained, and used for determination of Mg in a control sample. Results were compared with the results obtained using standard analytical technique, inductively coupled plasma emission spectroscopy (ICP), and excellent agreement between LIBS and ICP results was obtained.

Geological samples

A TEA CO₂ laser based LIBS system was applied for the analysis of basalt samples under simulated Martian atmospheric conditions (CO₂ gas, pressure 9 mbar) [8]. Photograph of the plasma induced by pulsed TEA CO₂ laser radiation (peak intensity 56 MW cm⁻²) in front of the basalt surface is shown in Fig. 6. The plasma emission was strong for relatively long period of time, and the propagation length was relatively large (25-30 mm). Fig. 7a shows spectra obtained for selected wavelength regions. Sixteen elements present in the sample (Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Si, Sr, Ti, V, and Zr) were identified. The estimated limits of detection were comparable to those reported in the literature, Fig. 7b [14,15].

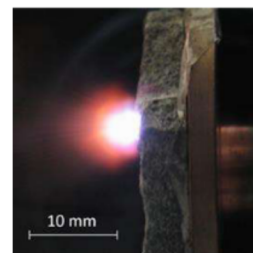


Figure 6. Plasma induced over basalt.

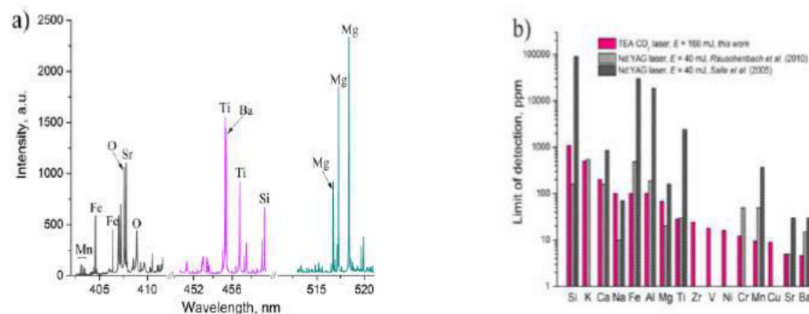


Figure 7. a) LIBS spectrum of basalt in a narrow spectral window. b) Comparison of LODs obtained with TEA CO₂ and Nd:YAG lasers.

Biological samples

The vast majority of LIBS applications deal with compact solid samples (homogeneous or structured) while analysis of powdered samples is less utilized. Compared to the analysis of compact solid samples, quantitative LIBS analysis of powdered samples is more easily achieved because of the possibility to prepare synthetic matrix-matching calibration standards.

TEA CO₂ laser based LIBS technique has been applied to the qualitative and quantitative analysis of macro and micro elements in commercial food supplement *Spirulina*. *Spirulina* is an edible photosynthetic multicellular cyanobacterium (blue-green algae) produced on a large scale to be used for animal and human nutrition, for pharmaceutical, biochemical and fertilizer products.

Results of qualitative analysis were compared to those obtained using a commercial LIBS system based on pulsed Nd:YAG. In general, 5 to 10 times higher analyte signals were measured in Nd:YAG plasma. Nevertheless, higher intensity of background continuum and background noise caused deterioration in the signal quality. Although of lower intensity, better resolved and sharper emission lines were obtained in CO₂ plasma. This may be attributed to relatively slow heating of the plasma (through absorption of the long lasting tail of the laser pulse), causing a larger and less-dense plasma plume and, therefore, less broadened lines. For quantitative analysis of metal content in *Spirulina*, laboratory produced matrix-matching calibration standards were used. Linear calibration curves were obtained for Ba (Fig. 9), Fe, Mg, Mn and Sr, with regression coefficients exceeding 0.92 and precision between 1.9 % (Ba) and 8.6 % (Sr). The estimated limits of detection were in the 0.1 ppm to 7 ppm concentration range, comparable to those reported in the literature.

CONCLUSION

Laser induced breakdown spectroscopy based on TEA CO₂ laser has been applied to elemental analysis of metals, geological and biological samples. A unique laser characteristics, the most important being the laser wavelength (10.6 μm) and the long lasting pulse tail (~2 μs), allowed successful application of time-integrated spatially resolved detection system for acquisition of emission spectra. Taking all into consideration: low-cost detection system; well-resolved, sharp spectral lines; minimal destructivity; good sensitivity; LODs in the ppm range, typical for LIBS, it can be concluded that the proposed LIBS system may be a suitable alternative to conventional LIBS that comprises Nd:YAG laser and time-gated detection.

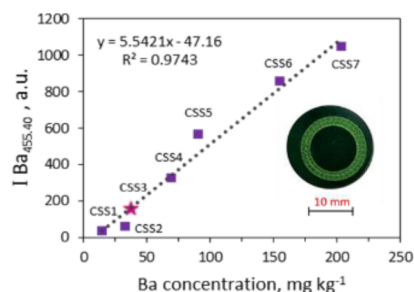


Figure 8. Calibration curve for Ba. Inset shows *Spirulina* sample pellet with clearly visible laser produced damages.

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