Spectrochimica Acta Part B 63 (2008) 1109–1116

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Optimization of micro-Laser Induced Breakdown Spectroscopy analysis and signal processing ☆

Pascal Robert *, Cécile Fabre, Jean Dubessy, Mickaël Flin, Marie-Christine Boiron

UMR 7566 G2R CNRS, Nancy Université, 54561 Vandoeuvre les Nancy, France

ARTICLE INFO

Article history:
Received 30 October 2007
Accepted 17 June 2008
Available online 27 June 2008

Keywords:
LIBS
Laser Induced Breakdown Spectroscopy
Time resolution
Signal processing
Signal to noise ratio

ABSTRACT

As a result of continuing instrumental development (Echelle spectrometer and ICCD detectors), micro-Laser Induced Breakdown Spectroscopy analysis may become an increasingly recognized analytical technique for determining elemental compositions of geologic materials. Best conditions of time resolution conditions (delay and time acquisition window) are estimated with respect to the collection geometry of optical plasma emission of our system. It turns out that the level of the Bremsstrahlung continuum emission is weak in the first tens of nanoseconds after the laser excitation pulse. The enlargement of the emission lines is identified in the first 100 ns but remains comparable to the spectral resolution of our system. Thus, results show that time-resolved conditions are not necessarily required to perform elemental analysis at the micrometric scale using LIBS, contrary to macro-LIBS. This suggests potential improvements of micro-LIBS analysis (sensitivity and spectral resolution) using non-intensified CCD connected with the laser pulse.
However, in order to improve the detection of weak signals obtained with an ICCD detector, working at high gain, a new method of signal processing on two-dimensional Echelle images has been developed. This method, based on the comparison of two 2D images, allows the identification of group of pixels (particles) that can be considered as representative of actual signals. This methodology applied to LIBS spectra eliminates the majority of noise peaks, allows the identification of weak signals which were almost impossible to extract from the noise, and does not alter the intensity ratio between emission lines. This method overcomes the poor dynamics of ICCD used at maximum gains and opens new possibilities in micro-LIBS analysis.

1. Introduction

During the last decades, advances in lasers, spectrographs and optical components have permitted to develop a new analytical technique based on LIBS (Laser Induced Breakdown Spectroscopy). Numerous references in the literature have yet reviewed the technical and analytical advantages of LIBS, demonstrating the potential of this analytical technique (numerous references in [1–3]). Some studies on micro-LIBS developments are also reported in [4–16]. Because we are working at the microscopic scale on heterogeneous samples, improvements of micro-LIBS analysis is required when only a very few number of signal acquisition is possible. Improvements have been focused in this work on acquisition time conditions and on signal processing in order to get the best data for quantitative analysis.

It is well known for so long that for macro-LIBS analysis obtained when the laser is focused onto the sample using a lens (typically of 50–100 mm focal distance), the Bremsstrahlung continuum emission and recombination radiations in the early stages of the plasma evolution are intense [17–19]. This feature justifies the use of ICCD detector to do time-resolved acquisition of the signal, characterized by a delay after the laser pulse and a time window acquisition. The first aim of this paper consists to investigate the variation of the intensity due to the Bremsstrahlung continuum emission as a function of the delay to define the best analytical conditions.

In micro-LIBS analysis, the amount of ablated matter and correlatively of excited matter, present in the plasma, gives rise to light emission less intense than in macro-plasma. The consequence is a lesser number of photons and a weak signal that requires the use of an ICCD working at high gain. The drawback of working at high gain is the high level of noise which makes difficult to identify a weak signal assigned to elements at low concentration. In addition, the heterogeneity of samples at the scale of tens of micrometer, specially geological samples, makes impossible the use of a large number of spectra (100) obtained from a section (100 μm × 100 μm) of the sample to improve signal to noise ratio: only a small number of LIBS spectra are available. Therefore, the second aim of this paper is to propose a signal processing method using a small

☆ This paper was presented at the Euro Mediterranean Symposium on Laser Induced Breakdown Spectroscopy (EMSLIBS 2007) held in Paris (France), 11–13 September 2007, and is published in the Special Issue of Spectrochimica Acta Part B, dedicated to that conference.

* Corresponding author. Tel.: +33 3 83 68 47 16; fax: +33 3 83 68 47 01.
E-mail address: pascal.robert@g2r.uhp-nancy.fr (P. Robert).

0584-8547/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.sab.2008.06.002

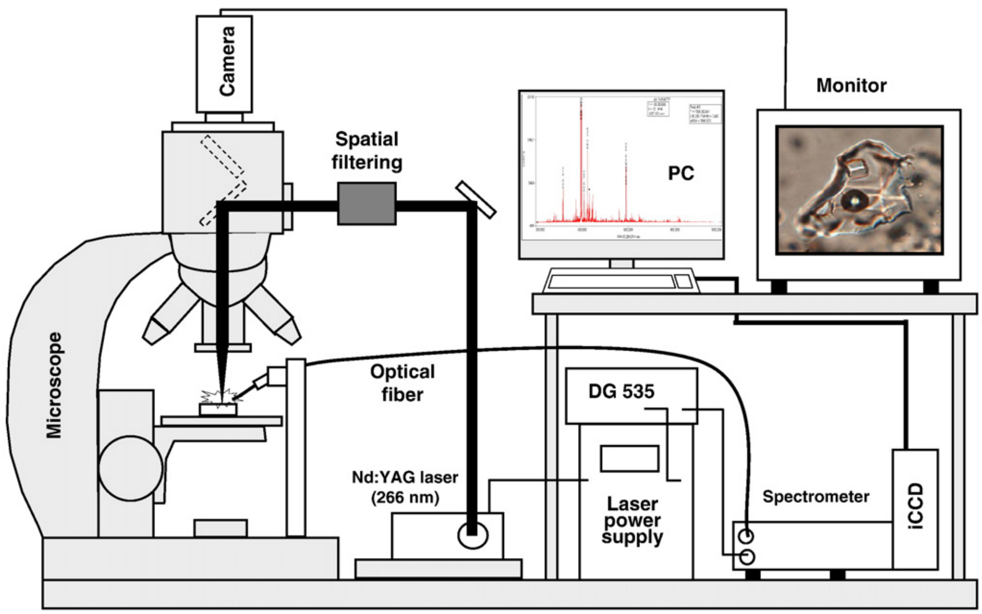

Fig. 1. Schematic representation of the experimental setup for the micro-LIBS experiments.

number of acquisitions ($2<n<10$) allowing a significant improvement of the signal to noise ratio.

2. Instrumentation

The apparatus was built in collaboration with the LRSI (CEA, France) and the company Optique Peter (Lyon, France) to carry out micro-analysis (between 5 and 10 µm diameter) of chosen parts of materials using optical observations with a microscope under transmitted or reflected light. This system is very close to those developed for micro-LIBS in [5,11]. This LIBS apparatus consists of a compact laser source quadrupled in frequency (Nd:YAG), a microscope (BX51, Olympus), a spectrograph and an intensified camera (Fig. 1). The analysis is carried out under atmospheric environmental conditions, without using any other gas flux. The selection of the micrometric part of the sample to analyze is made using the optical microscope with its magnified image on a TV monitor (PVM-145E, Sony) coupled with a TV camera (Cohu, Olympus) through a zoom. The laser source is a 50 mJ, 4-ns pulse, Nd:YAG laser (model Minilite II, Continuum) used at its fourth harmonic (266 nm) with a nominal delivered energy of around 4 mJ for a single laser pulse. Laser fluence is estimated to be around 5000 J/cm^2. The laser can be used either at 10 Hz repetition rate or more commonly at single pulse. Synchronization details between the laser and the ICCD are given below. In order to optimize the spatial resolution of the ablation, the laser beam is spatially filtered by focusing the laser through a 45 µm diameter hole with a 50 mm focal length lens.

An achromatic mirror objective with a long working distance (24.5 mm) is coupled with a mirror objective (25×, N.A. = 0.28, Ealing, UK) displaying a light reflection of 97% efficiency in the 250–700 nm range. Collection of plasma emission light is made using a needle optical fiber, at around 45° from the microscope optical axis and located at short distance from the micro-plasma (around 500 µm). The

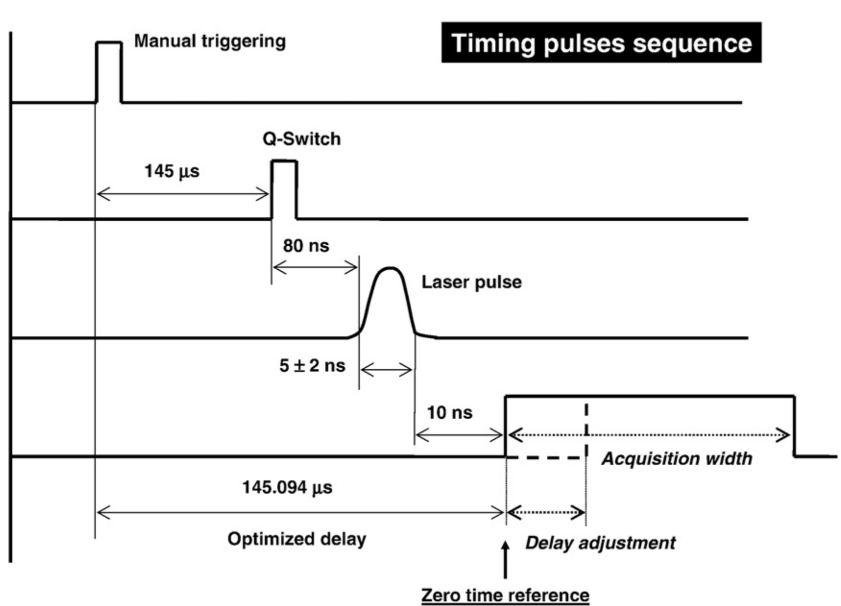

Fig. 2. Schematic representation of the temporal resolution options. Time scale is distorted; pulses and peaks are drawn wide for clarity.