CHEM 517

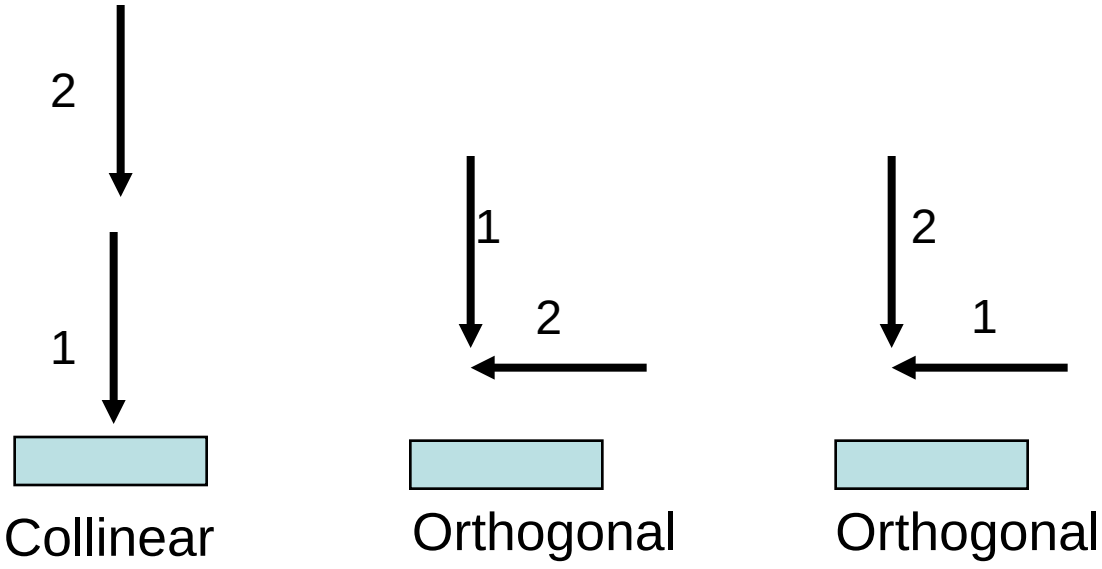
Fundamentals And Applications of Laser Induced Breakdown Spectroscopy, LIBS

CHAPTER VI

-DOUBLE/DUAL PULSE LIBS

TWO SEQUENTIAL PULSES :

SAMPLING GEOMETRY:



1 Laser for ablation
2 Laser for reheating/preablation

Collinear case:

In perpendicular configuration the laser is fired twice on the same spot on the specimen with a pulse separation in the order of one to a couple of tens of microseconds. Depending on pulse separation, the second pulse is more or less absorbed by the plasma plume caused by the previous pulse, resulting in a reheating of the laser plasma leading to signal enhancement

Orthogonal case:

A laser pulse is fired parallel to the sample surface either before or after the perpendicular pulse hits the specimen. The laser plasma ignited in the surrounding medium above the surface by a first pulse causes (by its shock wave) an area of reduced pressure above the specimen into which the actual plasma from the sample can expand. This has similar positive effects on sensitivity like LIBS performed at reduced pressures. If the orthogonal laser pulse is delayed with respect to the perpendicular one, the effects are similar as in the perpendicular configuration.

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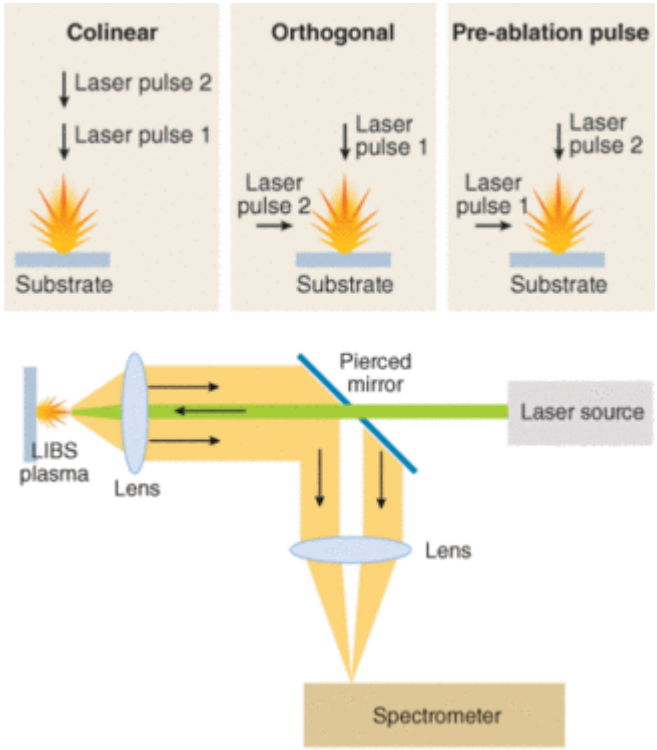

FIGURE 2. In "double-pulse" LIBS configurations with back-collection optics an initial laser pulse is followed by a secondary pulse that further enhances the emission of the ablated plasma plume from a sample under test (top). A typical back-collection LIBS optical setup includes optics, a laser source, and a spectrometer (bottom).

TWO SEQUENTIAL PULSES :

LASER TYPE:

- Pulse wavelength
  - UV followed by VIS, IR: 266nm, 532 nm, 1064 nm
  - IR followed by IR: 1064 nm, 1064 nm
- pulse duration
  - Femtosecond, nanosecond

Double vs Dual Pulse LIBS:

- Double Pulse LIBS
  - Two pulse from a single laser
- Dual Pulse LIBS
  - Two pulse from 2 different laser

- A single laser is preferred
  - in beam size,
  - complexity, and
  - beam alignment

✓a single resonator double pulse laser demonstrating full control over
- ✓ the pulse separation,
- ✓ relative intensities of first to second pulse, and
- ✓ pulse duration

provides a unique tool for LIBS characterization and optimization,

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SPECTROCHIMICA ACTA PART B

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Review

Double pulse laser ablation and plasma: Laser induced breakdown spectroscopy signal enhancement

V.I. Babushok [a,*], F.C. DeLucia Jr. [b], J.L. Gottfried [b], C.A. Munson [b], A.W. Miziolek [b]

[a] *National Institute of Standards and Technology, Gaithersburg, MD 20899, USA*
[b] *Army Research Laboratory, Aberdeen Proving Ground, MD 21005, USA*

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Facts about DP-LIBS*

- Double pulse LIBS is an effective way of enhancing the emission line intensities and improving the analytical capabilities of LIBS. Technique presents a more temporally effective means of delivering energy to the plasma and target surface.

- Several configurations of double pulse LIBS have been suggested. From the practical point of view, collinear double pulse LIBS is the simplest, effective realization of the double pulse procedure, providing easy access to the target surface. The best emission enhancement has been demonstrated with an orthogonal pre-ablation configuration.

- The different combinations of laser beam geometries, wavelengths, pulse durations, energies and interpulse delay time can be effectively used for the optimization of double pulse LIBS performance.

- Dual pulse laser ablation is used for the enhancement and optimization of many different characteristics of the laser ablation process; i.e., emission line intensities, characteristic decay time, ablation rate, ion density, crater size and shape, plume expansion rate, deposition properties, etc.

- Depending on the considered characteristic of the ablation process, maximum enhancement effects were observed at different separation times between pulses, ranging from the ps level up to the hundred μs level. Available experimental data demonstrate that the optimum separation times for maximum enhancement of LIBS emission are in the range from 0.2 μs to 30 μs for typical buffer gases (air, argon) and ambient pressure.

** V. I. Babushok, F.C. DeLucia Jr., J.L.Gottfried, C.A. Munson, A.W. Miziolek, Spectrochimica Acta Part B, 61 (2006) 999-1014*

Facts about DP-LIBS, Cont'd

- The enhancement of plasma emission depends on
  - the target material,
  - laser pulse characteristics,
  - ambient atmosphere and
  - interpulse delay.
- It was observed that the optimum inter-pulse delay is larger for ionic species than for neutral atoms. This is most likely due to the reduced density environment caused by the first laser pulse.

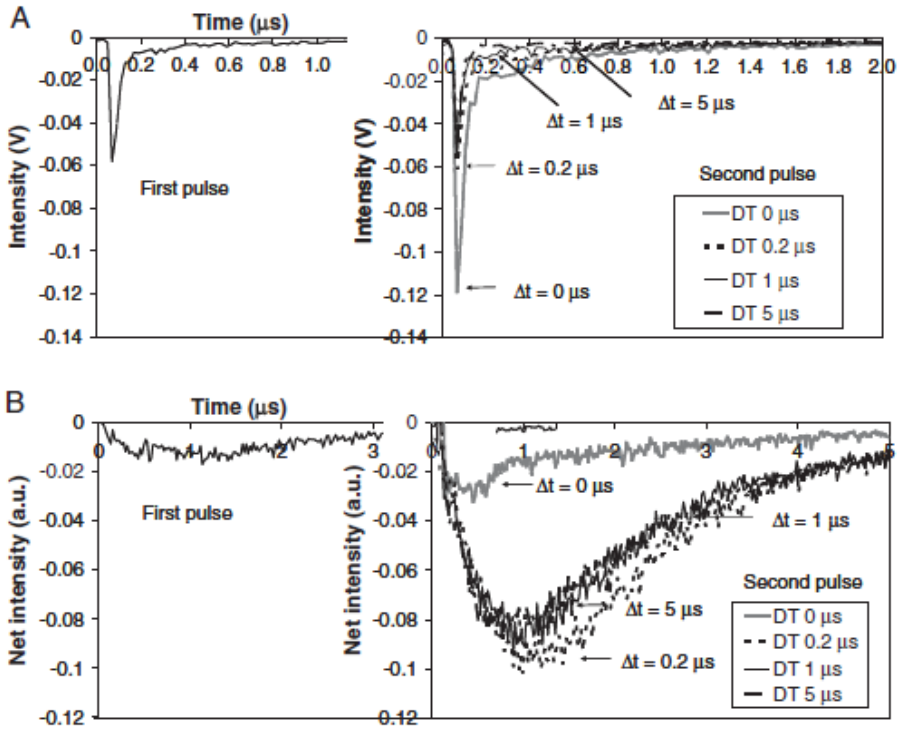

Fig. 2. Time profiles of the background (287.4nm) (A) and the Si I (288.16nm) line (B) obtained with a photomultiplier tube in the double-pulse approach DP 55+55mJ for synthetic glass (delay between the two laser pulses Δt=0, 0.2, 1 and 5μs).

- It was experimentally found that the enhancement factor is increased with increase in the energy of the excitation level.

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Facts about DP-LIBS, Cont'd

- Several suggestions regarding the mechanism of the enhancement effect of double laser pulses have been proposed in the literature. It may be that, depending on conditions and the process stage, different mechanisms are responsible for the enhancement effect with the use of different delay times.

- It seems likely that the second pulse provides the revival of plasma emission after the first pulse through increased rates of electron impact excitation, additionally ablated material in the gas phase and increased plasma volume. The enhancement effect is probably the result of the increase in the plasma plume volume after the second pulse and the decreased plasma density after the first pulse.

- Double pulse LIBS increases the
  - plasma volume,
  - temperature,
  - ion density in the plasma kernel,
  - the expansion and ablation rates, and
  - the decay time of line intensities,

  thus leading to the enhancement of emission line intensities.

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SPECTROCHIMICA ACTA PART B

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Applications of the double-pulse laser-induced breakdown spectroscopy (LIBS) in the collinear beam geometry to the elemental analysis of different materials

Céline Gautier [a,*], Pascal Fichet [a], Denis Menut [a], Jean Dubessy [b]

[a] *CEA (Commissariat à l'Energie Atomique) Saclay, Nuclear Energy Division, LRSI (Laboratoire de Réactivité des Surfaces et des Interfaces), Bâtiment 391, 91191 Gif-sur-Yvette, France*

[b] *CREGU-G2R UMR 7566, Université Henri Poincaré, Nancy 1, BP 239, 54501 Vandoeuvre-lès-Nancy Cedex, France*

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Abstract

Double-pulse laser-induced breakdown spectroscopy studies were performed on different types of materials (synthetic glasses, rocks, steels). Two Nd:YAG lasers emitting at 532 nm were combined in the collinear beam geometry to carry out double-pulse experiments at atmospheric pressure in air. For all matrices, the influence of the delay between the two laser pulses was systematically investigated from temporal and spectral analyses. Furthermore, the correlation between the excitation energy levels of the emission lines and the increases in intensity induced by the double-pulse scheme was described for each material. A comparison of the studies displayed different behaviors of the materials in the double-pulse experiments. An interpretation of the results is provided on the basis of the determination of the plasma temperatures in the single- and double-pulse configuration with the Saha–Boltzmann plot method. It also gave an insight into the potentialities and the limitations of the double-pulse laser-induced breakdown spectroscopy (LIBS) for analytical purpose so that the materials can be classified in terms of effectiveness of the double-pulse approach.

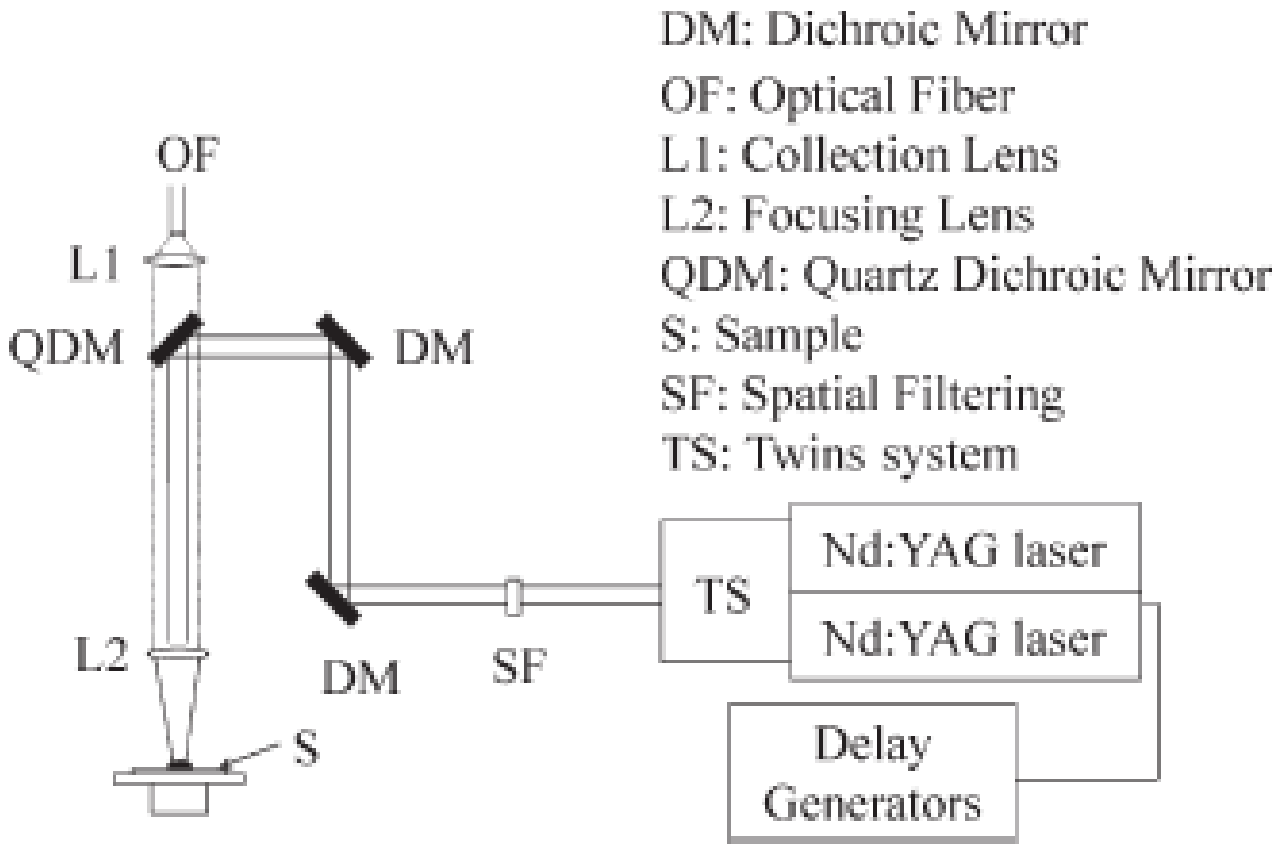

Fig. 1. Schematic diagram of the experimental setup for the double-pulse experiments in the collinear geometry.

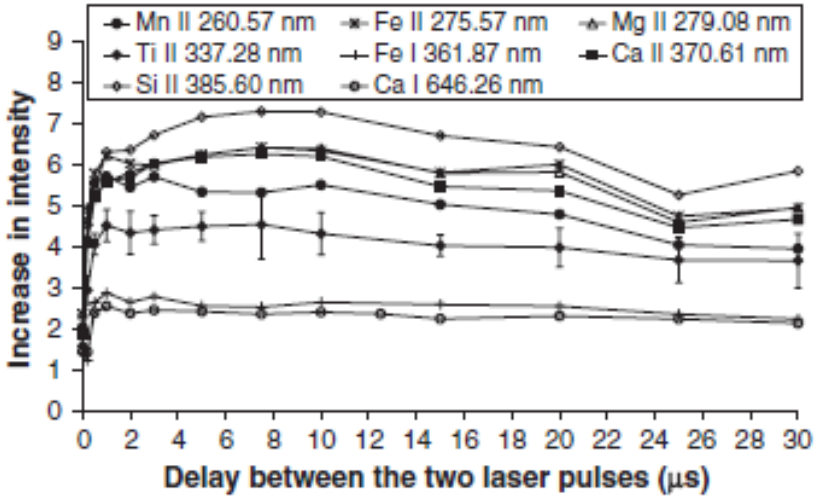

Fig. 3. Increase in intensity for a selection of lines detected from a synthetic glass as a function of the delay between the two laser pulses Δt recorded from the ESA 3000 echelle spectrometer (energy for each pulse: 55 mJ; gate width t_w: 30 μs; gate delay time t_d: 1 μs; exposure time: 1 s).

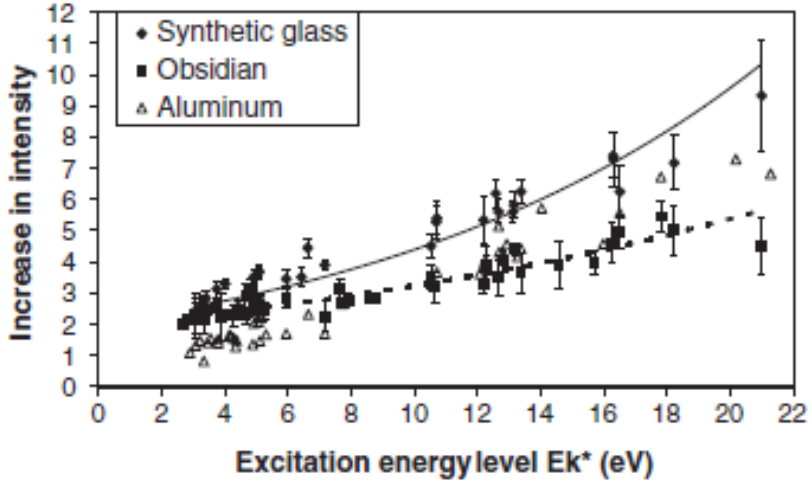

Fig. 4. Correlation between the increases in intensity of emission lines and their excitation energy levels in the double-pulse scheme (DP 55 + 55 mJ − Δt = 5 μs) for synthetic glass, obsidian and aluminum (data from Ref. [20] for aluminum) and modeling results (straight line for synthetic glass and regular-dotted line for obsidian) (energy for each pulse: 55 mJ; gate width t_w: 30 μs; gate delay time t_d: 1 μs; exposure time: 1 s).

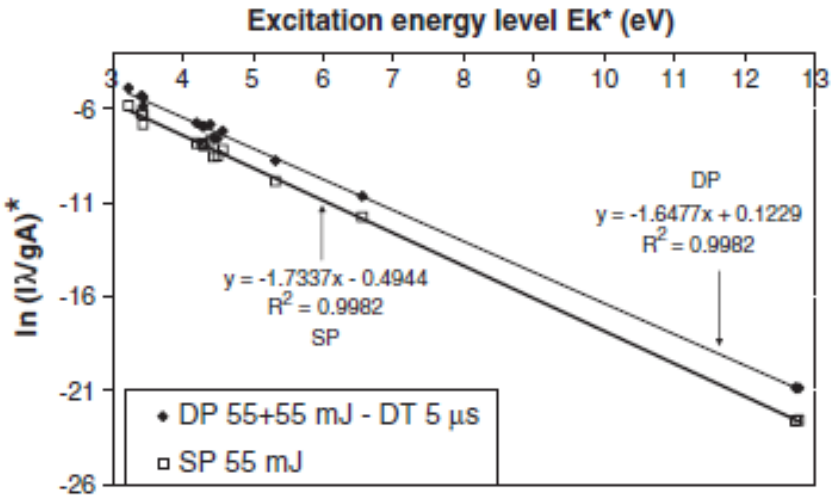

Fig. 5. Saha–Boltzmann plots obtained with Fe I and Fe II lines using synthetic glasses in the single-pulse experiments SP 55 mJ (thick line) and in the double-pulse experiments DP 55+55 mJ − Δt = 5 µs (thin line).

- For synthetic glass, the plasma temperature obtained in the double-pulse scheme DP 55+55mJ−Δt=5μs was approximately 4% higher in comparison to the one obtained in the single-pulse scheme SP 55mJ estimated at 6700K.

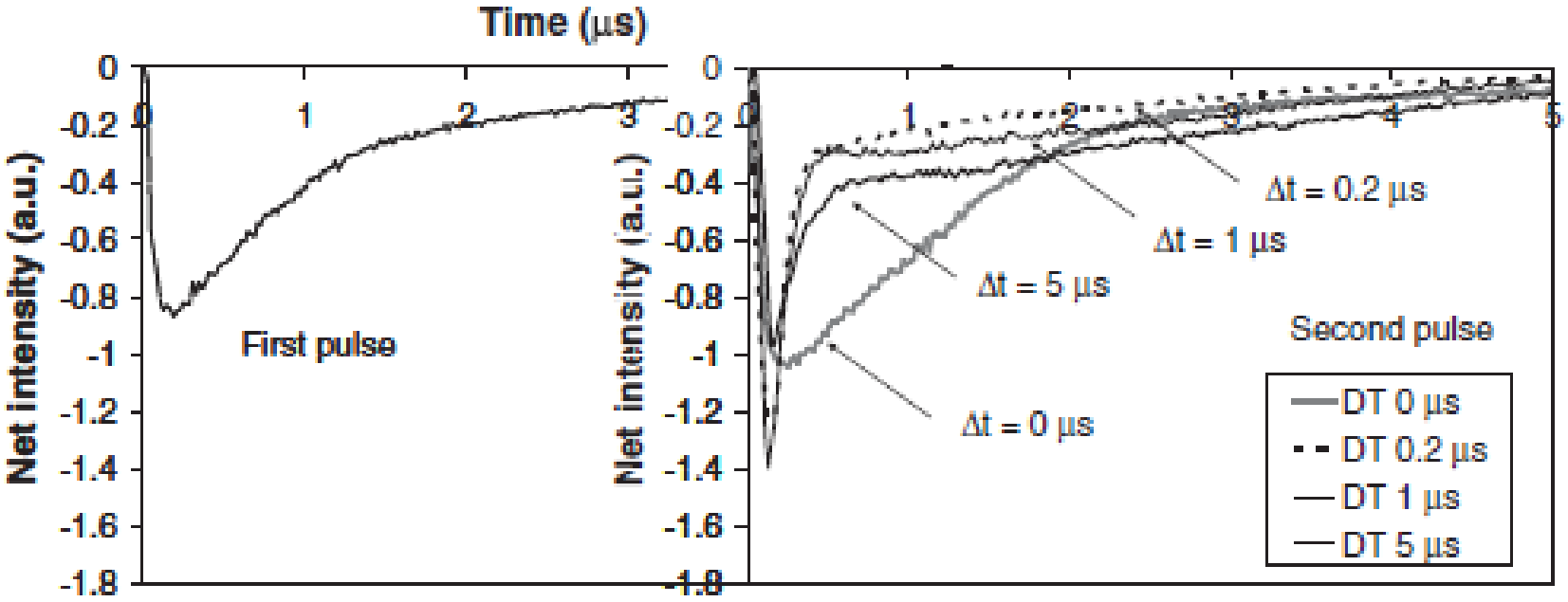

Fig. 9. Time profiles of the Fe II (275.55nm) line obtained with a photomultiplier tube in the double-pulse approach (DP 110+110mJ) (delay between the two laser pulses Δt=0, 0.2, 1 and 5µs).

Fig. 9 illustrates the time profiles of the Fe II (275.55nm) line for the double-pulse experiments DP 110+110mJ for different interpulse delays (Δt=0, 0.2, 1, 5µs) for a steel sample. In comparison to the first pulse, one can observe a change of behavior of the Fe II (275.55nm) line in the double-pulse approach for Δt>0µs. For an interpulse delay Δt>1µs, a slight increase in intensity of the Fe II (275.55nm) line can be noted for a delay time higher than 2µs. The hypothesis of a threshold of effectiveness for the double-pulse technique seems to be suitable for steels. It should be interesting to continue the optimization of the laser energy for each pulse.

Conclusion:

• This work enables to better understand the results previously reported in the literature on the double-pulse LIBS technique.

• The investigations undertaken on the different types of materials (aluminum, glass, rock, steel) prove that the increases in intensity obtained with the double-pulse experiments depend on the matrix.

• The double-pulse approach ensures the preferential enhancement of the intensities of emission lines originated from high excitation energy levels for vitreous matrices (synthetic glass, obsidian) and for aluminum. But, in the same conditions, the intensities of the emission lines with high excitation energy levels and detected from steels are not very much affected by the double-pulse experiments.

• Consequently, from the present experimental setup, the materials can be classified according to a decreasing order of effectiveness of the double-pulse approach: synthetic glass>aluminum>rock>steel. The potentialities of the double-pulse LIBS technique may be announced towards vitreous matrices containing elements emitting lines from high excitation energy levels, such as halogens.

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Fs/ns-dual-pulse orthogonal geometry plasma plume reheating for copper-based-alloys analysis

A. Santagata [a,*], A. De Bonis [b], P. Villani [a,b], R. Teghil [b], G.P. Parisi [a]

[a] CNR-IMIP, Sezione di Potenza, Zona Industriale di Tito Scalo, 85050 Tito Scalo (PZ), Italy
[b] Università degli Studi della Basilicata, Dipartimento di Chimica, Via N. Sauro 85, 85100 Potenza, Italy

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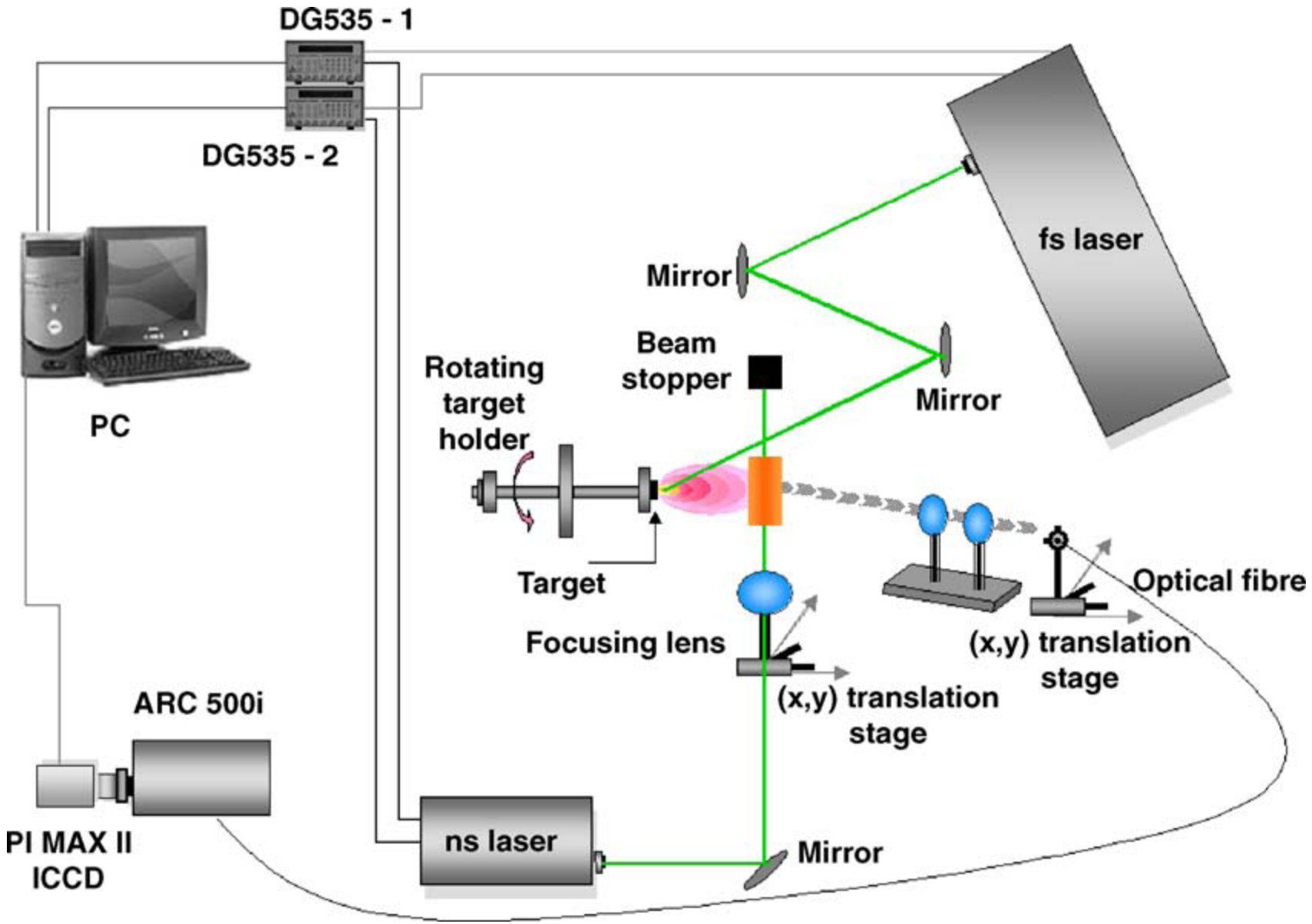
Abstract

Plasma plume emission spectroscopy signal enhancements between 12- and 280-fold were obtained in air at atmospheric pressure by reheating the fs-laser ablation plume (energy 0.75 and 3.0 mJ) with a 45 mJ ns-pulse in orthogonal geometry. The emission enhancements induced by the double pulse configuration (DP) at various inter-pulse delay times and distances of the second laser beam from the target surface were investigated for copper-based-alloy standards. Temporal surveys of the plasma plume temperatures induced by both fs-single pulse (fs-SP) and DP placed at a fixed distance of 0.5 mm from the target surface were carried out. Several copper-based-alloy standards were employed for drawing Zn calibration curves by using either fs-SP or DP configurations and considering Cu as internal standard. The experimental data show that, for high Zn contents, the fs-SP set-up is affected by a self-absorption phenomenon so that a deviation from the assumed calibration single linear response is observed and two linear regressions are considered. Conversely, it has been observed that the DP configuration is not affected by any self-absorption effect and provides an improvement of the Zn limit of detection (LOD) but worse calibration linear regressions than the fs-SP. Thus, the DP scheme can increase the analytical sensitivity of fs-SP and, furthermore, its process can be supposed to be independent from the matrix composition even for largely different Zn contents of the Cu-based-alloy standards used.


DG535 - 1
DG535 - 2
PC
fs laser
Mirror
Beam stopper
Mirror
Rotating target holder
Target
Focusing lens
(x,y) translation stage
Optical fibre
(x,y) translation stage
ARC 500i
PI MAX II ICCD
ns laser
Mirror

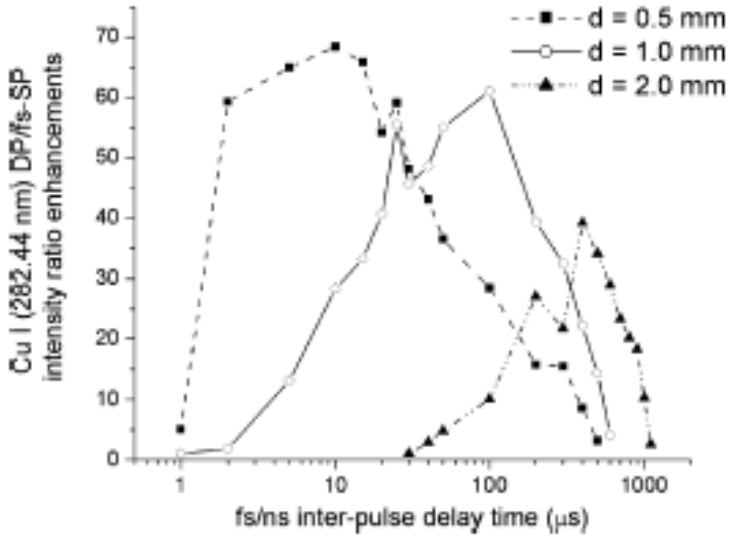


Fig. 2. DP/fs-SP intensity ratio enhancements of the Cu I (282.44 nm) line emission obtained at different fs/ns inter-pulse delay times and distances from the sample surface of the ns-pulse (detector gate = 0.5 μs).

- The fs/ns interpulse delay time as well as the distance of the ns-reheating laser beam from the target surface were varied between 1 and 1000 ms and 0.5 and 2 mm, respectively.
- It was experimentally evaluated that the ns-reheating pulse placed at a distance of 0.5 mm did not cause any secondary ablation processes of the target material.

The emission spectra acquired for performing such survey were obtained by 5 ms gate of the ICCD detector and by employing the HPb standard sample. It is clearly shown that the larger enhancement is obtained at a distance of 0.5 mm
of the ns-reheating pulse. At this distance, the DP showed an optimum inter-pulse delay time range between 2 and 25 ms with about 50–70-fold enhancements. Even at a distance of 1.0 and 2.0 mm, the DP intensity was characterized by not negligible improvements. It should be noted that by increasing the distance between the target and the reheating pulse, a less efficient interaction between the expanding plasma volume and
the ns reheating beam could be expected as a consequence of a lower density of the plasma involved.

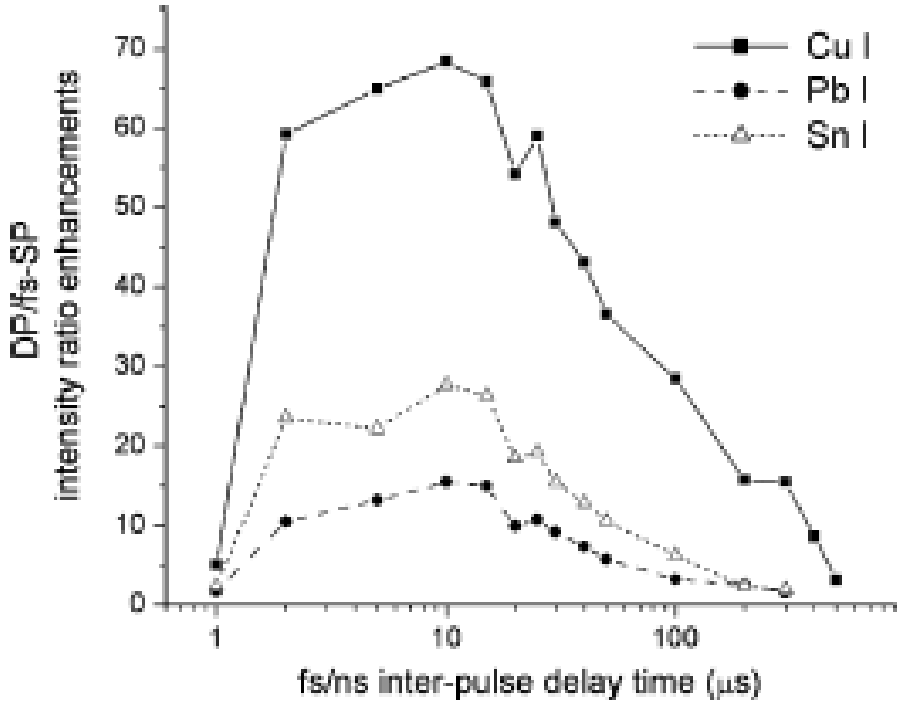
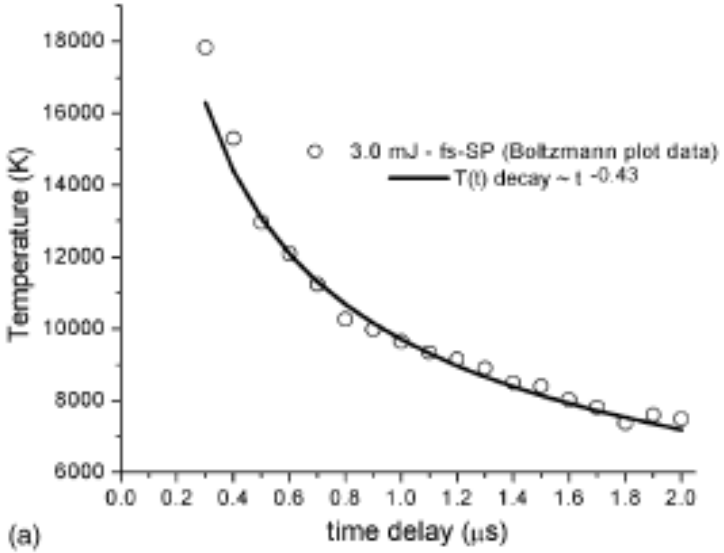


Fig. 3. DP/fs-SP intensity ratio enhancements of the Cu I (282.44 nm), Sn I (284.00 nm) and Pb I (280.20 nm) line emissions obtained at a distance of 0.5 mm of the ns-pulse and different fs/ns inter-pulse delay times (detector gate = 0.5 μs).

Fig. 3 shows the emission intensity improvements induced by DP on these lines together with the one occurring for Cu I at 282.44 nm. It shows that for inter-pulse delays of 2–25 ms the Pb and Sn emission maximum enhancements are between 10- and 30-fold. For discriminating the most stable working inter-pulse delay time in the range of 2–25 ms, the pulse-to-pulse Sn/Cu and Pb/Cu
signal ratios were considered. Our results showed that 10 ms was the most suitable inter-pulse delay time when 0.75 mJ of the first fs laser pulse energy was used. By employing 3.0 mJ of the fs laser beam, the same behaviour was observed, although an inter-pulse delay of 8 ms should be considered.



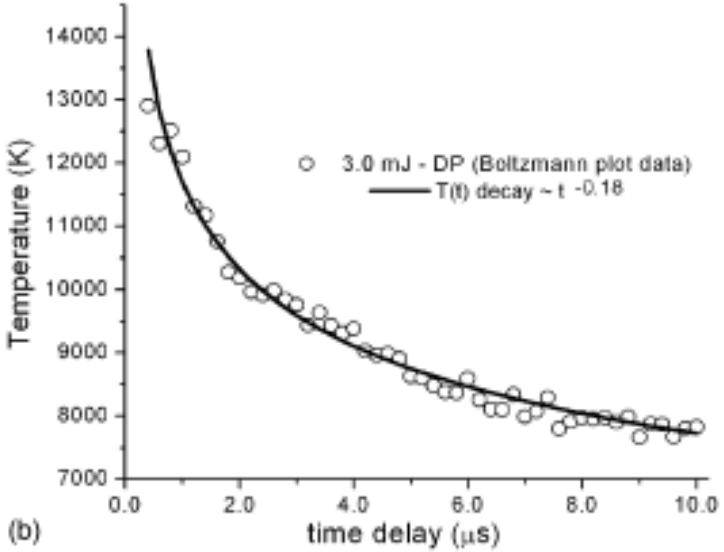


Fig. 4. Cu I excitation temperature decay of: (a) 3.0 mJ—fs-SP induced plasma (detector gate = 0.1 μs, time step increment = 0.1 μs) and (b) 3.0 mJ—DP induced plasma (detector gate = 0.1 μs, time step increment = 0.2 μs, ns-pulse distance = 0.5 mm); used sample: HPb.

The results reported in Fig. 4a show that during the fs-SP induced plasma the excitation temperature reaches about 18,000 K in the first hundreds of ns and then rapidly drops down proportionally to $t^{-0.43}$. This behaviour is in accordance with other fs-induced plasma temporal decays obtained by different
experimental set-ups and target materials [7,36]. After about 1.5–2.0 μs, the fs-SP induced plasma reaches a temperature plateau of 8000±300 K which can explain the low line emission intensities observed for longer delay times.

On the other hand, the DP induced plasma line emission intensities last for roughly 50 μs and this is certainly due to its slow temporal decay of the temperature proportional to $t^{-0.18}$, as shown in Fig. 4b where the temperature remains at about 8000 ±300 K even for relatively long time delays (6.5–10.0 μs). Therefore, it can be assumed that the plasma plume induced by the first fspulse can efficiently be reheated by the second ns laser pulse of the DP configuration sustaining for longer times high excitation
temperatures of the plasma so that a larger ICCD gate width can be employed and emission intensities enhancements are achieved.

Conclusions:

• As a relevant remark, the DP configuration here realized is characterized by a pretty slow excitation temperature temporal decay of the plasma ($t^{-0.18}$) providing emissions lines lasting longer than those occurring for fs-SP ($t^{-0.43}$).
• The experimental results here presented have thus shown that an orthogonal configuration ns-pulse can provide an efficient reheating of a fs induced plasma.
• This effect conveys a relevant enhancement of the fs-SP emission signal intensities supplying a significant improvement of the relative Zn LODs. With this regard, further progresses can likely be achieved by varying the reheating pulse features, the optical emission collecting system configuration, the ICCD acquisition set-ups and the Zn I line to be investigated.
• As a drawback, the DP configuration here realized is characterized by slightly worse calibration curves than the fs-SP ones as a consequence of appreciable emission line shot-to-shot fluctuations probably due to the lack of fully reproducible air breakdown induced by the reheating ns laser pulse.
•Despite of this, the DP configuration shows negligible self-absorption effects even when the ablated material composition does change significantly, making this approach suitable for analytical applications even for large variations of the matrix composition.
• Further works are required by considering alternative experimental set-ups and environmental buffer gasses and pressures for actually establishing the DP independence from the sample matrix and for minimizing the emission signal fluctuations here observed.

Summary :

- ✓1 to 2 orders of magnitude enhancement in signal intensity
- ✓The mechanism by which the pre-ablation pulse caused enhanced ablation is due to
  - ✓ sample heating
  - ✓ lowering the pressure above the sample surface
  - ✓ increasing N_e above the surface
  - ✓ interaction of the expanding shock on the surface
- ✓Both double-pulse LIBS as well as LIBS at reduced pressures are aimed at
  - ✓increasing the sensitivity of LIBS
  - ✓reducing errors caused by the differential volatility of elements (e.g. Hydrogen as an impurity in solids).
  - ✓It also significantly reduces the matrix effects.
  - ✓Double-pulsed systems are also proving useful in conducting analysis in liquids, as the initial laser pulse forms a cavity bubble in which the second pulse acts on the evaporated material.

Suggested Reading materials:

Double pulse laser ablation and plasma: Laser Induced breakdown spectroscopy signal enhancement
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Review paper

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Applications of the double-pulse laser-induced breakdown spectroscopy (LIBS) in the collinear beam geometry to the elemental analysis of different materials, Céline Gautier ,Pascal Fichet, Denis Menut, Jean Dubessy
Spectrochimica Acta Part B 61 (2006) 210–219

Time-dependent single and double pulse laser-induced breakdown spectroscopy of chromium in liquid
Virendra N. Rai, Fang Yu Yueh, and Jagdish P. Singh
Applied Optics, Vol. 47, Issue 31, pp. G21-G29 doi:10.1364/AO.47.000G21

http://www.laserfocusworld.com/articles/248140