Insights into Enhanced Repeatability of Femtosecond Laser-Induced Plasmas

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ABSTRACT: Repeatability is of utmost importance as it is directly linked to measurement accuracy and precision of a technique and affects its cost, utility, and commercialization. The present paper contributes to explain enhanced repeatability of the femtosecond laser-induced breakdown spectroscopy (fs-LIBS) technique, remarkably significant for its industrial applications and instrumental size reduction. A fs-laser with 7 mJ pulse energy was focused to create a transient titanium plasma, and a high-resolution spectrometer was used to study time-resolved spectra and single-shot drilling sampling repeatability. Time-resolved spectroscopy study at a delay time interval of 0−1600 ns showed 200−400 ns as the optimum delay time zone for data acquisition with 2−4% line intensity RSDs. Plasma temperature RSDs were <1.8% for the investigated delay interval and reached 0.5% at 200 ns where the temperature recorded a maximum value of 22,000 K. Electron density reached 5.7×10^{17} cm^{−3} at 200 ns, and RSDs were <3% with the least fluctuation of 0.7%. Shot-to-shot RSDs were 3.5−5% at 15−30 drilling shot intervals for line intensities, <2% for plasma temperature, and <6.5% for electron density. Using an uncertainty propagation formula, total number density RSDs were calculated to be 1.9−5.3% for 50 single-shot drilling scenarios. Considering physics behind results, fs-plasmas are “stable ablation sources” due to their electrostatic formation mechanisms and confined hydrodynamic evolution. The fs-laser opens up new directions for LIBS applications where accuracy is significantly enhanced.

INTRODUCTION

With developing chirped-pulse amplification, powerful femtosecond laser systems have been constructed and introduced into laser-induced breakdown spectroscopy (LIBS). Femtosecond lasers can improve figures of merit for LIBS analytical performance, including the absence of fractional evaporation, better depth control and quality ablation crater, reduction in damage, and better reproducibility. The booming growth of LIBS commercialization and attention toward high accuracy and precision makes repeatability, reproducibility, and measurement uncertainty so far of significant importance. Shot-to-shot repeatability is an important aspect for a precise quantitative performance of any laser-based technique. Repeatability is the precision with which a test can be repeated under the same experimental conditions (shot-to-shot or intrameasurement precision). At different experimental circumstances, reproducibility determines the precision with which a test can be performed (or intermeasurement precision). For single-event microanalysis applications, where femtosecond laser-induced breakdown spectroscopy (fs-LIBS) competes with other techniques with a feedback ablation-analysis loop, all the required data is obtained from only one laser shot. Under such desideratum, reproducibility is strictly required and hence understanding uncertainty sources inside fs-plumes.

Among different laser parameters that affect the laser ablation process, pulse duration is the most virtual one due to substantially contrastive physics of energy deposition in the fs regime. Femtosecond irradiation has a pulse duration shorter than both the electron−lattice relaxation time (\(t_{el-latt}\)) and the heat conduction time (\(t_{cond}\)): \(t_{el} \ll t_{cond} \approx t_{heat} \approx 1−10\) ps. Therefore, fs-laser pulse interacts only with the electron subsystem and energy deposition happens via inverse Bremsstrahlung at the very beginning of irradiation deposition, which does not obey Fermi−Dirac distribution in the absorption region (~10 nm in depth). Photoinduced electrons overcome the potential barrier due to multiphoton absorption as the typical barrier energy exceeds photon energy.
RESULTS AND DISCUSSION

Time-Resolved Emission of Ti-fs-LIPs. Temporal evolution of spectral lines reflects the resoluteness of atoms, ions, and molecules in excited states within the plasma. The objective of this experiment was to understand the physics behind line evolution and to observe optimum delay for data acquisition. For performing such a procedure, delay time has been changed, covering a time range between 0 and 1600 ns at 100 ns steps. The gate width was fixed at 100 ns, which was sufficient to obtain a rich spectrum from a train-pulse ablation (100 accumulated pulses). The normalized spectra emitted by the plasma in the spectral window of 250–433 nm at 400 and 1600 ns delays are shown in Figure 1. A static analysis of the spectral lines showed a large population of both neutral and ionic lines. This is in contrast to several research studies while dominancy of atomic lines was reported.26–28 Abundant
emission of atomic and ionic lines can be explained by effective atomization (the absence of fractional vaporization) and effective excitation (high electron temperature) within the plasma. An intense emission region was observed, which was shifted to the IR region from UV with increasing delay despite identical ablation and optical collection conditions. This trend is consistent with the temporal decay of the plasma where low energy transitions are persistent at longer delays. It is worth noting that the overall intensity of the whole spectrum at 1600 ns delay was ∼3 times lower than the intensity at 400 ns delay.

The absence of fractional vaporization was confirmed as the employed system delivers a power density of $0.2 \times 10^{17}$ W cm$^{-2}$ upon focusing, referring to a laser fluence of >20 J cm$^{-2}$, which is far higher than threshold ablation fluences for elements in the sample matrix. Further, a train pulse irradiation is reported to decrease the ablation threshold fluence due to an incubation phenomenon according to

$$F_{\text{Th}}(N) = F_{\text{Th}}(1)N^{-\xi}$$

where $F_{\text{Th}}(1)$ is the single-pulse threshold fluence and $\xi$ is the incubation parameter. This decrease is attributed to the formation of laser-induced states where energy deposition increases (material fatigue) and creation of laser-induced defects where surface modifications (surface ripples and nanocracking) upon applying pulses increase as well. Meanwhile, surface reflectivity was observed to significantly decline after the first few pulses in a train ablation. Surface and crater patterning was observed using surface profilometry for a train pulse of 100 accumulated pulses. The crater diameter was ∼250 μm, and its depth was ∼25 μm with the presence of ripple structure inside it, captured by a scanning electron microscope, as shown in Figure 2. In spite of the fact that threshold fluence reduction favors effective ionization, the changeable energy dissipation seems to cause fluctuated ablation within the burst. It is worth noting that fs-pulses in a train are temporally separated from each other by ∼1 ms (repetition rate is 1 kHz) and a separate ablation process is acquired with each interaction. Previous studies revealed that

![Figure 2. Surface profilometer image of the Ti sample after pulse-train ablation of 100 shots. The crater diameter was ∼250 μm, and its depth was ∼25 μm. Surface ripples and nanocracking were captured by scanning electron microscopy.](image1)

![Figure 3. Time evolution of (a) normalized intensities of V I 233.449, V II 304.667, Ti II 315.418, and Ti I 390.476 nm lines through a delay interval of 0−1600 ns shows three different temporal evolutions; (b) corresponding RSDs for 20 measurements.](image2)
accumulated pulses within a fs-train showed less matrix dependency with increasing laser repetition rate. Therefore, accumulation of repeated signals within the pulse train accounted for increased ablation uncertainties and, moreover, obtained less matrix-dependent and high-intensity signals (better signal-to-noise ratio).

Raw spectra were analyzed and among 900 defined lines; 54 lines were selected as well-resolved, non-resonant, and free of spectral interference. Spectral lines were identified from the NIST database. Figure 3 depicts the temporal evolution of normalized intensities and corresponding RSDs of four lines (V I 233.449 nm, V II 304.667 nm, Ti II 315.418 nm, and Ti I 390.476 nm) from the Ti alloy sample (TC4-1, 89.63% Ti, 5.65% V). The integrated intensities of 20 surface shots, each refers to 100 accumulated fs pulses at 1 kHz, were normalized to the maximum of each line in order to compare the evolution distribution of different emitters on the same scale. All lines were processed by calculating the peak area after background subtraction. Different atomic and ionic lines marked a slightly different optimum delay time for each species in the plasma matrix and followed one of the three evolution behaviors. As shown in Figure 3a, intensities increase within the delay interval of 0–200 ns followed by maximum intensities in the 200–400 ns delay interval and a decay afterward. Line intensities peaked and decayed differently depending on the evolved line. The atomic line V I 233.449 nm showed the highest normalized intensity at 200 ns followed by a fast decay. This line corresponds to a high energy transition (ΔE = 42,823 cm⁻¹), which requires high plasma temperature formed at the early stages of evolution. Both ionic lines V II 304.667 nm and Ti II 315.418 nm showed highest intensities at 300 and 400 ns, respectively, and moderate decay for longer delays. Ionic line decay behavior is attributed to energetic electron–ion recombination. The neutral line Ti I 390.476 nm (ΔE = 25,602 cm⁻¹) showed both gradual increase in the time interval of 0–400 ns and gradual decrease afterward, maintaining a persistent lifetime of >1 µs.

The fs-plasma evolves and decays much faster than ps/ps-plasmas. For 500 ns, after the laser strikes the material, ns-plasma kinetic energy is mainly spent in compressing the surrounding air and forming a shock wave. At this stage, the ns-spectrum is dominated by continuum radiation with no information to be collected precisely. This 500 ns time regime seems long enough for the fs-plasma to evolve with band-shaped spectral lines over a low continuum all at the first 200–400 ns. Commonly, in ns-LIBS, delaying data acquisition with respect to laser firing to avoid the overwhelming continuum radiation and to suppress spectral interference due to line broadening costs ~1–1.5 µs at optimized experimental configurations. Results reported for a ps-train showed that 700 ns was consumed by continuum emission to reduce a background emission level. While ps/ps-plasmas’ absorptivity diminishes markedly to change the opacity from optically thick into transparent thin media, the fs-plasma lacks any kind of “plasma shielding” or “laser trail-plasma interaction” which dominantly makes its evolution a confined and stable event. Extra morphological fluctuations caused by ns-post-ablation interactions were reported as a significant source for chaotic plasma generation and opacity. Signal uncertainty is basically assigned to this first-formed laser-plume event at delays of 500–800 ns and to the total number density fluctuation in consequence. At fs-pulse trail, extensively hot electron gas and undistributed lattice are ready for interaction. Adiabatic expansion seems to happen after the fs-laser strikes the sample due to Coulomb explosion and confined dynamical behavior dominates the kinetics. The ablated material explodes in so-called “cool ablation” and the number of ions created in the first stage of ablation can only decrease with recombination. Fs-uncertainty emanates basically from energy–material coupling, which causes changes in ablated mass and haywire electrostatic collisions within the plume, which are discussed hereinafter.

Signals’ repeatability, i.e., RSDs, takes an inverse of that for normalized intensities in a general sense (see Figure 3b). RSDs first slightly decreased within 100 ns and then fluctuate as the plasma continued to evolve in the time interval of 200–400 ns with 2–4% fluctuation. RSDs of fs-evolution provide evidence of high repeatability compared to ns/ps-plasma plumes at early stages (data are only processed with background subtraction). The V I 233.449 nm line had the lowest fluctuation over the time interval of 200–400 ns relative to all other lines, while its RSD increased drastically after 400 ns to reach ~15% for a 1600 ns delay time. This is consistent with its fast evolution and short lifetime. Both V II 304.667 nm and Ti II 315.418 nm lines had slightly increasing and fluctuating character with RSDs in the range of 2–4% (and not more than 5% for some delay measurements). The Ti I 390.476 nm showed steady RSD values ~2% for most investigated delays. It is worth
mentioning that RSDs of line intensities at 200 ns showed unexplained one-trend fluctuation (~3 times higher) and this should be related to local changes of the sample properties like physical defect, dust, or human errors. To maintain idea fluency, these results have not been plotted. From an analytical point of view, there existed an optimal temporal window for detection, within which high signal intensities and low RSDs are recorded. Based on results, the optimum delay time zone is 200–400 ns, and so, 400 ns was chosen for a single-shot repeatability study experiment to encounter high uncertainty of short-lived lines, observe repeatability of stable lines, and ensure the absence of continuum contribution. 

**Time-Resolved Plasma Parameters.** Plasma parameters are well-suited signature of its physics. Spectral line characteristics (intensities, resolution, widths, and repeatability) are related to the matter chemical structure, plasma properties, and precision of the analytical information. Figure 4a,b shows the temporal evolution of plasma temperature and electron density and corresponding RSDs at the same studied delay interval (0–1600 ns). The gate width for each acquisition is 100 ns, and the delay step increase is 100 ns. Excitation temperature was calculated using integral line intensities with the Boltzmann plot method, assuming plume species are in LTE (local thermodynamic equilibrium) as:

\[
\ln \left( \frac{\lambda_{ki}}{g_i A_{ki}} \right) = - \frac{E_k}{k_B T} + C
\]

where \( \lambda_{ki} \), \( I_{ki} \), \( g_i \), \( A_{ki} \), \( E_k \), \( k_B \), and \( C \) are the emission wavelength, integral intensity of emission line, degeneracy of upper-level energy, transition probability, upper-level energy, Boltzmann constant, and constant, respectively. Plasma temperature was obtained using the slope of the fitted line. Non-resonant V II lines were selected to deduce the temperature. Spectral line parameters were extracted from the NIST database and are listed in Table 1.

| \( \lambda_{\text{nm}} \) | \( E_k/\text{eV} \) | \( E_i/\text{eV} \) | \( A_{ki}/\text{s}^{-1} \) | \( g_i \) | \( g_0 \) |
|----------------------|------------------|------------------|------------------|------|------|
| 253.46               | 6.29             | 1.40             | 3.5 \times 10^{-07} | 3    | 1    |
| 255.58               | 6.52             | 1.67             | 3.9 \times 10^{-07} | 3    | 5    |
| 257.09               | 9.47             | 4.65             | 9.0 \times 10^{-07} | 5    | 7    |
| 281.02               | 6.69             | 2.28             | 1.5 \times 10^{-08} | 7    | 7    |
| 301.71               | 5.81             | 1.70             | 1.29 \times 10^{-08} | 5    | 7    |
| 396.83               | 4.52             | 1.40             | 6.5 \times 10^{-06}  | 3    | 1    |

The electron density was determined by using the FWHM of spectral lines according to Stark broadening:

\[
N_e = \frac{\Delta \lambda_{\text{Stark}} \times 10^{16}}{2 \alpha}
\]

where \( \alpha \) is the electron impact parameter and \( \Delta \lambda_{\text{Stark}} \) is the FWHM of the Stark broadened profile. Lines’ profiles are affected by different broadening mechanisms. Stark broadening and instrumental broadening are accounted for in laser-induced plasmas, considering that contribution of other broadening mechanisms is ignorable. The Ti II transition at 302.97 nm was used for electron density measurement and was fitted using a Voigt profile, which considers Stark broadening by Lorentzian and instrumental broadening by a Gaussian profile. Stark broadening was deconvoluted after inserting instrumental broadening (measured to be 22 pm using a mercury lamp) as follows:

\[
\Delta \lambda_{\text{measured(Voigt)}} = \left[ \left( \Delta \lambda_{\text{Stark(Lorentz)}} \right)^2 + \left( \Delta \lambda_{\text{Instru.(Gauss)}} \right)^2 \right]^{1/2}
\]

As depicted in Figure 4, at a 200 ns delay time, both plasma temperature and electron density reached their maximum followed by fast decay. Similar decay trends for both temperature and electron density were observed except that temperature showed a slightly faster decay. The highest plasma temperature recorded 22,000 K at 200 ns. This is consistent with line intensities peaked at the same delay, corresponding to high-energy transitions. Temperature varied from 22,000 to 14,000 K, which is higher than ionization energies for elements in the sample matrix confirming effective atomization and ionization within the plasma. Even at longer delays with strong spectral presence (plasma cooling), the temperature maintained values >10,000 K, which supported the claim of energy, heat, and pressure confinement in fs-plumes due to its evolution hydrodynamics. Plasma temperature RSDs were <1.8% for the studied delays, indicating quite stable plasma heat content repeated in 20 different ablations for all delays. The least RSD was observed at 200 ns with 0.5%. Plasma temperature RSDs gradually increased after 600 ns. Plasma cooling is described to be a chaotic process with the production of aerosols formed by agglomerates of small blackbody-like nanoparticles with low kinetic energy. This cooling process is reported to occur after 500 ns of fs-laser firing in vacuum via radiative cooling of electronically excited atomic and ionic species through collisions. Elastic and inelastic collisions happen inside high-density plasmas formed by tightly focused fs-lasers where electrons, ions, and atoms presumably collide via recombination, ionization, ion-charge interchange (disproportionation), and radiation relaxation (and/or trapping) reactions as follows:

\[
S^n+ + e = S^{(n-1)+}
\]

\[
S^n+ + e = S^{(n+1)+} + 2e
\]

\[
S^n+ + S^{+} = S^{n+} + S^{(n+1)-} + \hbar \nu
\]

\[
S^{n+} = S^{++} + \hbar \nu
\]

where S refers to atomic/ionic species. These reactions, mainly with unknown rate constants, yield an overall decrease in electron density. Head-on collisions between atoms at small distances from the sample surface could produce collisional-induced excitation (and even ionization) of one or both colliding particles. If an atom with mass \( M_i \) is traveling with kinetic energy \( E_k \) and collides with a stationary atom of mass \( M_e \), then the maximum fraction of energy transferred into the internal energy of either colliding species is:

\[
f = \frac{\Delta E_k}{E_k} = \frac{M_i}{M_i + M_e}
\]
which gives $f \approx 63.4\%$ for Ti–Al collisions and $f \approx 46.2\%$ for Ti–Fe collisions. Nonetheless, unpredictability of such inelastic collisions makes these energy fractions a considered source of plasma temperature fluctuations. In fs-ablation, electrons play a vital role in peak power/energy deposition mechanism and plume evolution via photon–electron interaction, electron–lattice interaction, and plasma evolution dynamics. Upon laser firing, a highly excited electron cloud is formed on the sample surface where electronic temperature is stabilized by electron–electron scattering and non-thermalized electrons undergo ballistic transport as well. Heat diffusion from electrons to lattice occurs via electron–phonon coupling, and a two-temperature model is used to describe the energy balance process as follows:

$$C_e \left( \frac{\partial T_e}{\partial t} \right) = \frac{1}{\rho_e c_v} \left( \frac{\partial}{\partial x} \left( k_e \frac{\partial T_e}{\partial x} \right) \right) - G_0(T_e - T_l) + S_{lase}(x, t) \left( \frac{\partial T_l}{\partial t} \right),$$

where $C_e$ and $C_l$ are electron and lattice heat capacities, $T_e$ and $T_l$ are electron and lattice temperatures, $k_e$ is the electron thermal conductivity, $G_0$ is the energy coupling factor, and $S_{lase}(x, t)$ is a source term. In particular, despite the fact that lattice temperature evolution seems to depend on energy coupling and electron–lattice interaction, plasma evolution is continually modeled to fully understand plume dynamics after electron thermalization.46

Although heat diffusion between the electron cloud and lattice occurs in a 10ps time scale, simulations of plasma dynamics showed that kinetic processes suggest changes of electronic temperature and density on time scale of a few hundred picoseconds.30 Figure 4, our spectroscopic approach showed that the electron density increased from $5.4 \times 10^{17}$ to $5.7 \times 10^{17}$ cm$^{-3}$ in 200 ns. Fine time-resolved spectroscopy study in a 0–200 ns delay time interval can be useful to observe electronic dynamics and emission uncertainties within. Electron density RSDs were <4% and hit the least fluctuation at 800 ns with 0.7%. Considering that the 600 ns delay is a plasma cooling stage, electron density maintained RSDs >1% through its dynamical evolution. In view of the foregoing, however, in fs-laser power deposition, hot energetic electrons cause specific ablation of ejecta, non-equilibrium electron distribution, and unpredicted elastic and inelastic collisions inside each formed plume cause uncertainties in electron density.

**Shot-to-Shot Repeatability.** Repeatability is the most significant with single-shot LIBS applications.48 A variety of factors affect shot-to-shot repeatability, on top of the list are laser energy coupling with sample and stability of plasma parameters (source noise33). Variations in the ablated mass per laser shot are the main contributor to signal fluctuations indeed. Surface heterogeneity, texture, and roughness affect the laser energy coupling contributing to change in ablated mass per laser shot. In the current experiment, surface smoothness was carefully accounted for to minimize surface alterations effect prior to the experiment. To estimate single-shot repeatability, line intensities of the selected 54 lines were plotted as a function of the shot number. Scan matrices consisted of 50 positions $\times$ 50 drilling shots, i.e., a total of 2500 shots. The experiment was conducted using a 400 ns delay time and 1000 ns gate width.

Figure 5 represents intensity and RSDs variation obtained from V I 337.753 nm and Ti II 333.520 nm lines as a function of laser drilling shot number. Overall, intensity slightly decreases for the first five shots and then gradually increases from 5th shot up to 25th shot. For more drilling, intensity forms a plateau, which tends to decrease with shots more than 35. The studied atomic and ionic lines showed different intensity values with drilling. The atomic line intensity increased up to 15th shot then formed a plateau between 15 and 30 shot number and then distinctly decreased afterward. Shot-to-shot RSDs were least at 10–30 drilling shots and increased fast with more drilling. Meanwhile, for the ionic line, intensity plateau started at 25th shot and line intensities tended to decrease after 35th shot. Shot-to-shot RSDs were least at 18–32 drilling shots and increased gradually with more drilling. This is explained with surface morphological alterations with drilling. For initial few shots (~5 as results depicted), the sample surface incubates cracks, ripples, and

![Figure 5](https://dx.doi.org/10.1021/acsomega.0c03636)
laser-induced periodic melt,\textsuperscript{49} which decreased laser energy deposition (and consequently line intensity, plasma temperature, and electron density). With further drilling, confined plasma formed in a cavity maintained a higher temperature and favors ionic line population. Therefore, RSDs on both sides of the “least fluctuated interval” had an opposite behavior for the atomic and ionic lines; for the atomic line, RSDs were higher after the stable drilling zone, while for the ionic line, RSDs were higher before. Shot-to-shot RSDs are 3.5–5% at 15–30 drilling shot intervals. One might consider that optical collection system efficiency should add fluctuations due to the formation of plasma on a level lower than the optimum field of view with drilling. Results are consistent with a previous study in comparison between single-shot and raster ablation modes of fs-LIBS;\textsuperscript{37} an increase-plateau-decrease behavior was observed for the single-shot drilling mode relative to constant intensity for the raster one (100 shots for both modes). The single-shot plateaus was observed after 10 laser shots, and signal fluctuation increased dramatically after 35 laser shots. Generally, pulse-to-pulse RSDs for raw data using ns-lasers on metal samples record >10%\textsuperscript{50} as the total ablated mass variability fluctuates with dominant thermal ablation mechanisms.\textsuperscript{3} It is worth noting that RSDs in the case of 100 shot drilling mode were lower compared to single-shot analysis mode owing to $n^{3/2}$ dependence\textsuperscript{5} of RSDs on the number of accumulations, despite the overall uncertainty increase by pulse-train as described in the previous section. The trade-offs between stable average ablated mass per shot and plasma confinement mechanism are important to optimize fs-reproductibility.

**Single-Shot Plasma Parameters Repeatability.** Pulse-to-pulse variations can be understood by the following plasma parameters. Plasma temperature variations affect plasma species dynamics and degree of ionization and yield changeable emission intensities due to redistribution of species energy levels. Electron density variations reflect alterations in plasma dynamics. For quantification purposes, plasma parameters can be dependent on to compensate for total number density uncertainties via modeling. Herein, plasma temperature and electron density were calculated to study plasma physics variations with drilling up to 50 shots (delay time was 400 ns and gate width was 1000 ns).

Figure 6 shows that, initially, plasma temperature decreased, attributed to dissipated heat for crater formation. The subsequent semilinear increase up to 30th shot is ascribed to plasma confinement followed by a plateau, which may be the result of a trade-off between plasma confinement and energy deposition efficiency inside the crater. Electron density showed a decrease–increase trend up to 30th drilling shot similar to plasma temperature behavior. The decrease in the electron density afterward indicates a decrease in ablation efficiency and an increase in recombination processes. RSDs were <2% (except at 36 and 45 shots) for plasma temperature and <6.5% for electron densities. Besides plasma dynamics uncertainties, calculating plasma temperature carried onboard mathematical errors of spectroscopic parameters. Transition probability, for instance, was reported to exhibit standard deviations of 5–50%.\textsuperscript{51} Yet, errors in line fitting and electron impact parameter added errors to electron density RSDs. The evolving trends of both plasma temperature and electron density as well as corresponding RSDs confirmed line intensity evolution and stability depicted in Figure S at the 10–30 drilling zone.

Based on the Saha–Langmuir equation,\textsuperscript{52} line intensities are affected by plasma temperature $T_p$, electron density $N_e$, and total number density $N_t$, while the latter is proportional to the total ablated mass. Uncertainties of the three physical parameters contribute, differently though, to spectral line fluctuations. To get an estimate for ablated mass fluctuations for the single-shot drilling strategy, a mathematical uncertainty propagation formula\textsuperscript{53} can be used to compute propagated error in a function of several variables as

$$\delta I = \left\{ \left( \frac{\partial I}{\partial T_p} \right)^2 (\delta T_p)^2 + \left( \frac{\partial I}{\partial N_e} \right)^2 (\delta N_e)^2 + \left( \frac{\partial I}{\partial N_t} \right)^2 (\delta N_t)^2 \right\}^{1/2}$$

where $\delta I$ is the total uncertainty in a spectrally detected line intensity. Utilizing Ti II transition at 302.97 nm, uncertainties in the total number density was sorted out to be in the range of 1.9–5.3% for a single-shot ablation scenario. Nevertheless, in a few number of shots, electron density uncertainty term $(\partial I / \partial N_e)^2 (\delta N_e)^2$ exceeded the overall line intensity RSD, making the estimation of the total number density uncertainty to be negative values. Shot-to-shot repeatability experiment was conducted at a 400 ns delay time. Thus, evaluation of relative contributions of $T_p$, $N_e$, and $N_t$ to the total intensity uncertainty at different delay times in parallel with investigating 0–200 ns delay time plasma dynamics via time-resolved spectroscopy should provide a guideline for enhanced...
Time-resolved spectra and shot-to-shot reproducibility were studied to underlie the fs-physics behind signal stability and to investigate uncertainty sources. Self-induced fs-LIBS repeatability is attributed to the (1) relatively stable nature of plasma evolution due to electrostatic ablation, i.e., Coulomb explosion; (2) stable average ablated mass per shot, which is dramatically related to the less heat affected zone, and hence, no splashing nature of the ablated material; and (3) high repetition rate operation of the fs-laser, which allows accumulation of repeated signals within a burst and improves reproducibility by $n^{1/2}$. The fast evolution of fs-plasma and the absence of laser—plume and plume—plume interactions bring new aspects of improving repeatability and data acquisition. With such stable plasma evolution and low continuum radiation, emission spectra can be recorded in non-gated modes using portable spectrometers. Enhanced single-shot repeatability of fs-LIBS promotes the technique accuracy needed to consider it a truly quantitative technique. Uncertainty sources are outlined as follows: (1) energy coupling fluctuations due to the thermal response of the irradiated electronic system. Electron—phonon collisions and scattering are, in a realistic picture, fluctuated intermediates to couple laser energy into the lattice; (2) elastic and inelastic collisions inside the plasma, which changes plasma density due to electron—ion recombination and undesired excitation and/or ionization; (3) threshold fluence fluctuations due to an incubation phenomenon; and (4) surface structure alterations due to the formation of cracks, ripples, and laser-induced periodic melt with multiple pulse ablation, both provoke changes in plasma parameters and hence ablated mass per shot. Based on previous long-term research to enhance ns-spectral data repeatability and with underlying physics behind fs-plume uncertainty, fs-LIBS can outdo accuracy and precision limitations of the technique. More investigations on fs-plume evolution physics and its corresponding analytical performance and advantages are required as short ways-out to shed light into new aspects in instrumentation (size, complexity, and cost of systems) and applications (especially industrial). This approach permits an extension into conditions not covered by experiments, underlying more background understanding, and contributes for developing a precise quantitative analytical model.

**EXPERIMENTAL SECTION**

Instrumental. The femtosecond laser system used is a one-box ultrafast Ti:Sapphire amplifier (Spectra Physics, USA) with 125 × 68 × 29 cm dimensions (see Figure 7). The laser system employs adjustment-free EternAlign optical mounts to maximize long-term stability and operation (energy stability of <0.5% rms over 24 h operation) and is capable of producing fs-pulses with an energy of 7 mJ and a pulse width of 45 fs at a 1 kHz repetition rate. The amplified laser pulses are centered at 800 nm with linear polarization. An intensity auto-correlator and a power meter periodically monitor the pulse width and energy drifts in order to ensure a stable energy flux at the target. The output laser beam is a TEM$_{00}$ Gaussian beam profile with a beam quality $M^2$ of <1.25 and a diameter of ~10 mm. The laser system includes two power supplies and chillers for seed (Mai Tai) and pump (Empower) lasers. The laser system was operated in a gated mode and fired by sending a command using external port of a delay generator (DG645, Stanford Research Systems, USA), which is used to synchronize both the laser and spectrometer. The laser beam was first reflected by three 730−820 nm ultrashort mirrors and then focused onto the sample surface by a plano-convex lens (fused silica, $f = 100$ mm, $d = 25$ mm, and 4.79 mm central thickness). The mirrors and focusing lens have graphed a group delay dispersion of ~0 and 36 fs$^2$ for wavelengths centered at 800 nm, respectively. Two plano-convex lenses (fused silica, $f = 50$ mm, and $d = 25$ mm) were used to collect the plasma emission light and focus it into an optical fiber at a 45° adjustment angle. The fiber guides the...
light to an Echelle spectrometer (Aryelle Butterfly, LTB, Germany). The spectrometer consists of two channels: 192–433 and 425–750 nm, which can be used alternatively with a spectral resolution of 13–31 pm. An intensified charge-coupled device (ICCD, Andor, 1024 × 1024 pixels) was used to detect the dispersed spectrum, and Sophi software was used to store data to a computer. All experiments were performed in an ambient environment (lab. temperature of ∼21–23 °C and humidity <20%). For each experimental set, the spectograph was wavelength calibrated using a mercury lamp (DH-3plus, Ocean Tec, USA).

Considerations about Fs-Laser Pulses. Several aspects have to be considered before firing fs-LIPs, including (1) Temporal structure of the fs-laser output peak intensity. Pre-and post-pulses are formed by Fresnel reflections in optical elements inside the regenerative amplifier cavity and greatly affect the laser–matter interaction. Particularly considered are pre-pulses that can create a plasma before the main pulse arrival,24 “shielding” its energy deposition into the sample. Careful reduction of pre-pulses incorporates an extra-cavity Pockels cell to make pulse selection and a combination of intracavity Pockels cell and a passive 1/4 waveplate to yield a contrast ratio of >1000:1 for output peak intensity to any prepulse that occurs >1 ns before the main output one; (2) Plasma-ignition threshold fluence ($F_{\text{th}}$). Although fs-ablation is proved to reduce the dependency on thermal properties of pure or alloyed samples and turned more correlation to work function,55 calculation of $F_{\text{th}}$ is required to ensure the absence of fractional evaporation especially for single-shot analysis scenarios; (3) Broadening of fs-pulse by an optical system. Ultrashort pulses with a Gaussian transform-limited propagation experience a duration lengthening after passing through a dispersive medium. The pulse broadening implies a reduction of the pulse peak intensity while keeping the measured pulse energy the same. The pulse content is critical for fs-LIBS as plasma kinetics is mainly controlled by power density dissipation mechanisms. Although these mechanisms are not still fully understood, it is of no doubt that marking group velocity dispersion (GVD) of the utilized optical system is a necessity. The output pulse width can be determined as follows:4,56

$$\tau = \tau_0 \sqrt{1 + \left( \frac{4 \times \ln 2 \times \text{GVD} \times l}{\tau_0^2} \right)^2}$$

where $\tau_0$ is the pulse width before passing the optical system and $l$ is the length of the dispersive medium. In the present setup, the initial 45 fs pulse experienced broadening to 46.24 fs before hitting the sample (small enough not to seriously alter the laser–matter interaction).

Sample Preparation. A standard titanium alloy sample TC4-1 was used in this study with composition 3.90 wt % Al, 5.65 wt % V, 0.39 wt % Fe, 0.277 wt % Si, and 0.158 wt % C. The sample was in a disk shape with stock dimensions 35 mm D × 36 mm H. The sample was mounted on a manually controlled 3D translation stage. Before each experiment, the sample was carefully polished by sandpapers (500, 800, 1200, and 2000 grit) to diminish surface impurities and was cleaned by ethyl alcohol to ensure surface cleanliness. Experiments were done by moving the sample to a fresh spot to avoid striking on the formed ablation zone. Surface topologies were studied using white-light interferometry (Zygo-NexView, Ametek, USA) and focused ion beam scanning electron microscopy (Lyra 3, TESCAN, Czech Republic) for ablation craters.

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