Efficient non-gated remote filament-induced breakdown spectroscopy of metallic sample

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Abstract

Remote filament-induced breakdown spectroscopy (R-FIBS) is a novel technique that could be applied at long distance up to a few kilometers. Our work demonstrates that by creating short and strong filaments in the atmosphere with a telescopic beam delivering system, continuum background in R-FIBS spectrum will be significantly reduced. This allows for a non-gated R-FIBS configuration for identifying solid targets. As an example, we used an aluminum plate located 50 m away from our detection system. The obtained fingerprint spectrum is so strong that the detection limit could reach 1.9 km in distance and ppm level in terms of minor element concentration.

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a rapid, real-time and multi-elemental analytical technique [1–3]. It involves focusing the output of a pulsed laser (conventionally a Q-switched nanosecond (ns) Nd:YAG laser) onto a material under test and generate luminous plasma. The light emitted by the plasma can be spectrally and temporally resolved to provide information on the elemental composition of the material. Due to its versatility, minimal sample preparation and simplicity, LIBS has been associated with a rapidly increasing list of applications [4,5]. Particularly, the remote LIBS has received special attentions [6–9] from the point of view that it is beneficial in many circumstances where the target samples are difficult to access or located in hazardous areas, such as biochem agents in the atmosphere [10], a nuclear-polluted industrial or urban site [11] and molten alloys in an industrial site [12,13]. The recent developments in the LIBS, including the employment of dual-pulse technique [14,15] and the introduction of Échelle spectrometer [16–18], have further brightened the future application of LIBS.

In addition, because of the growing popularity of femtosecond laser systems, femtosecond (fs) laser pulse has been studied as an alternative excitation laser source in LIBS. Lower ablation threshold, higher sensitivity and improved precision have been suggested to be the attractive properties of fs-LIBS [19,20]. Some researchers have considered the benefits of fs-LIBS in the framework of microanalysis [21,22]. Moreover, a number of results have demonstrated that by using fs-LIBS, the plasma continuum would be significantly reduced, making non-gated spectrum measurement available [19,22,23]. This is advantageous compared to the ns-LIBS, where the early developed plasma continuum is so dominant that one has to measure line emission with a time delay typically on the microsecond scale. Obviously, the employment of non-gated technique in fs-LIBS...
has several merits, such as reducing the complexity of the detection system and its cost, lowering the detection limit and making the system more compact [23,24].

Another breakthrough in fs-LIBS related work has recently been brought forward by the French and German consortium, the Teramobile group. They have successfully demonstrated the possibility of remote operation of fs-LIBS at distances up to 180 m by using femtosecond laser filaments in air [25–27]. This experimental scheme has been referred as remote filament-induced breakdown spectroscopy (R-FIBS). The outstanding characteristic of this technique is that in the course of filamentation in air, due to the dynamical balance between the optical Kerr self-focusing of the laser beam and the defocusing effect of the plasma generated through tunnel/multiphoton ionization of air molecules at the self-focus [28], the laser pulse could maintain high intensity, which is about \(5 \times 10^{13} \text{ W/cm}^2\) [29,30], even at a distance as far as a few kilometers [31]. This differentiates R-FIBS from traditional long pulse LIBS, where the laser focal diameter is linearly proportional to the distance leading to the difficulty in delivering high laser intensities over long distances. Naturally, R-FIBS has been recommended for kilometer-range applications [26].

Despite the great potential of R-FIBS, the efficiency of this technique will be one of the important concerns towards its maturity. In the current R-FIBS experiments, the multi-TW laser beam was often freely sent into open air. Because of the high peak power and modulation instability, multiple filaments will be unavoidably created. That would lead to multi-filamentation competition phenomenon [32]. The result is an unstable and weak emission signal requiring in real practice considerable accumulation time of the signal [25,32]. That might limit the applicable distance or prohibit the application where real-time measurement is necessary. Thus, a reliable scheme of controlling the filaments is demanded to induce efficient emission within the framework of R-FIBS.

Besides, the laser pulse will self-transform into a chirped white light laser (supercontinuum) during the filamentation [28,33]. The dramatically broadened spectrum spans from infrared (IR) to ultraviolet (UV) [34–36]. Thus, to avoid the interference of the scattered white light laser spectrum with the desired line emission signals, a gated detector was still required in the R-FIBS configuration. Though it has been mentioned that the UV components within the white light laser spectrum could be minimized through empirical optimization of the initial laser chirp, which allows for a non-gated spectrum measurement below 400 nm [26], it is still advisable to seek for some promising methods to implement a non-gated technique for the whole spectral range to further increase the efficiency and simplicity of the R-FIBS technique.

In the present work we discuss an inexpensive and effective way to approach both aims at the same time. Essentially, we have used a telescope as the beam delivering system to send our Ti:sapphire femtosecond laser system output pulse (centered at 800 nm) into a hallway to produce strong and short filaments at different distances [37]. It is well known that the shorter the filament is, the less broadened the spectrum of the laser will be [28]. Thus in this way, the white light laser spectrum is reduced significantly. Hence, in an equivalently non-gated configuration, we have successfully recorded intense and distinct signature spectrum from an industrial aluminum plate located 50 m away from the sending telescope. And for the first time, the ability of sensing minor elements by using R-FIBS technique is demonstrated as well.

2. Experiment and results

Our experimental setup is shown in Fig. 1. The telescope consists of a 5 cm diameter convex mirror, whose focal length is \(-50 \text{ cm}\), and a focusing lens with a focal length of 100 cm (diameter of 8 cm). After the telescope, the laser beam diameter was increased from 1.2 cm at full width at half maximum (FWHM) to about 2.5 cm (FWHM). In the current experiment, the energy of our laser pulse was fixed at 108 mJ/pulse and the pulse duration was negatively chirped to 10 ps. This pulse was then sent through a 100 m long corridor. Since its peak power (11 GW) was higher than the critical power for self-focusing (\(<5 \text{ GW}\)) in air [38], filamentation took place inside the corridor.

To perform the R-FIBS measurement, we set the effective focal length of our telescope to be 50 m as shown in Fig. 1. Filaments appeared in the vicinity of the geometrical focus with a total length of about 1 m. The formed filaments directly stroke on the surface of an aluminum alloy plate (6061-T6) provided by ALCAN, whose thickness was 0.5 cm with 2.5 cm in diameter. The aluminum plate was put approximately 10 cm after the beginning position of filamentation. In order to provide a nearly fresh surface for each shot, the sample was vertically installed on a rotating stage. A typical LIDAR (Light Detection And Ranging) setup [39] was established next to the telescope to collect the plasma light into a spectrometer (Acton, SpecPro-500i) equipped with an ICCD (intensified charge coupled device) camera (Princeton Instruments, PI-MAX-512). The spectral resolution of the spectrometer was about 0.4 nm when a grating of 1200 g/mm and 100 μm entrance slit were used. A 1 μs wide exposure gate, with \(t=-33 \text{ ns}\) delay with respect to the laser pulse arriving time on the target (\(t=0\)), was applied on the ICCD. This is equivalent to a non-gated experimental scheme. By only using moderate gain (40% of the maximum ability of the ICCD), the registered spectrum is demonstrated in

![Fig. 1. Experimental setup.](image-url)
Fig. 2, which is the result of 10 shots accumulation. Even though identifying all the spectral lines in Fig. 2 exceeds our current central interest, for the sake of future analysis, we have highlighted a few representative spectral lines. They have been assigned to Al I (394.4 nm, 396.15 nm) and Mg II (279.55 nm, 280.27 nm), respectively [40]. In Fig. 2, the signal beyond 700 nm would be masked by the back-scattered fundamental laser spectrum. Besides, our detection system was not sensitive to IR light. Therefore, IR spectrum was not investigated in our experiment.

3. Discussions

In so far as a non-gated technique was used, the attractive feature shown in Fig. 2 is the low level of continuum background over the whole spectral range studied. There are two reasons for that. First, fs-LIBS giving rise to low continuous background is a common experimental observation [19,22,23]. It is attributed to the relatively colder plasma and faster decay of the plasma continuum compared to the case of ns-LIBS [40]. It is necessary to point out that because of the self-compression phenomenon accompanied with the filamentation process, the pulse duration becomes appreciably shorter, with the possibility of reaching few-cycle regime [41–43]. Therefore, despite of the 10 ps initial pulse duration in our experiment, the fundamental interaction physics of R-LIBS would be similar to laboratory fs-LIBS. No evident plasma continuum should be expected.

The secondary potential source of continuous background comes from the scattered white light laser spectrum. To deal with this issue, we have to recall that the spectral broadening during filamentation is due to self-phase modulation (SPM) inside the filament [44,45]. The induced white light spectrum covers from 230 nm to 4 μm in air [33–35]. Nevertheless, SPM is linearly proportional to the propagation distance. And experimental evidence did show a progressive increase of the laser spectral width as a function of propagation distance [39]. It hints that shorter filaments will lead to higher contrast between the white light spectrum and the line emission spectra in the case of R-FIBS. However, the reported total lengths of filaments generally scale from a few tens of meters to hundreds of meters in the atmosphere, where terawatts (TW) level Ti:sapphire lasers are ordinarily used [46,47], inducing distinct white light generation [33].

To overcome the above mentioned obstacles, a telescope type beam delivery setup has been suggested [37,48]. This idea has been proved by our previous work to be successful in terms of freely moving the filament location and producing short filaments [37]. It was again confirmed by our on-site observation that the filaments were roughly 1 m in length at 50 m. On the other hand, the self-steepening effect would not be prominent in the sense that we chirped our pulses to a not-so-short duration of 10 ps in the experiment. Taking into account both factors, spectral broadening in our experimental scheme would be much less pronounced [37]. We notice that in Fig. 2, several spectral lines between 500 nm and 700 nm are in fact the second order diffraction of some UV lines. However, it would not affect our conclusion that the contribution of continuum background to our spectrum is non-substantial. This implies that non-gated spectrum acquisition for R-FIBS is feasible over a very wide spectral range apart from the fundamental light spectrum.

We note that if the sample was located at the beginning of a long filament, white light would also be weak. However, such a long filament generally implies free propagation of the pulse in which multi-filament competition takes place leading to unstable and weak fluorescence signal [32]. The current technique is preferable because it gives rise to exceptionally strong signal too. For example, the intensity of the strongest spectral line (Al I: 396.15 nm) in Fig. 2 is as high as 227,550 ICCD counts. Note that only moderate gain was used and the saturation point of the ICCD camera is 655,350 counts for 10 shots accumulation. Such a strong signal will certainly be appreciated for further applications of R-FIBS. In order to quantitatively elucidate the strength of our recorded signal, we have done the following estimations about the detection limit of our system.

The simplest one is to look for the ultimate distance, at which the same aluminum plate can be identified. According to the previous findings, the local R-FIBS signal is independent of distance [26,37] because the laser intensity is constant due to the intensity clamping inside the filament [29,30]. We consider that the back-scattered white light laser spectrum is also invariant when the distance changes. This assumption is valid as long as we keep the same relative distance between the target and the starting position of filament, since SPM then mainly depends on the clamped laser intensity inside the filament. So when distance R changes, the amount of the signal, S, collected by our Lidar system will obey the rule: \( S \propto 1/R^2 \) (in the case of low atmospheric absorption). Based on this knowledge, the intensity of Al I: 396.15 nm line versus distance has been plotted in Fig. 3(a) (black line). The criterion of 3σ will be adapted to define our detection limit. Here, σ is the standard deviation of the background spectrum which was taken experimentally under the same condition but without sending the laser pulse into the corridor. This background, hence, takes into account both the detector noise and the environment background. In Fig. 3(a), the 3σ level has been indicated by the
red line. According to this criterion, the maximum detectable distance is 1.9 km. This distance might even be extended by a few times if we apply the maximum gain on our ICCD camera. A secondary effort has been put into verifying the detection limit of the minor element concentration inside the sample. We first choose Mg as an example. The weight concentration of Mg in our aluminum 6061-T6 sample is 0.8%. Assuming that the signal intensity from minor element is linearly proportional to its concentration [40], we present in Fig. 3(b) the intensity of Mg II: 279.55 nm as a function of the element concentration (black line). The weak white light background has been subtracted in the calculation. Consequently, the 3σ criterion implies a detection limit of 0.0033%, i.e. about 33 ppm. It hints that a sensitivity of less than 1 ppm could be obtained if the detection distance is less than 10 m. Based on the same arguments, the detection limits of a few other analytes are listed in Table 1. It is worth mentioning that the detection limits listed in Table 1 are optimistic when we take into account that the white light spectrum has intrinsic modulation and may affect the determination of the noise level. However, it is not so straightforward in practice to isolate the white light spectrum completely from the obtained LIBS spectrum for the purpose of quantitative analysis. We have tried to roughly evaluate the influence of the white light background to our detection limit estimations. Our attempt is to replace σ with the standard deviation of the white light signal fluctuation (σ′) within a short wavelength range (268 nm–276 nm). This choice is based on the fact that it is near the interested Mg II: 279.55 nm line and there is no other spectral line present. The new 3σ′ level gives us a detection limit of 0.0081%. Though this value is more than two times higher than the datum in Table 1, it is still impressive considering that the sample was located 50 m away from the detection system.

The excellent detection sensitivity demonstrated in our experiment could be explained by the scenario of multiple filamentation competition [32,49,50]. It tells that multiple filaments produced by widely spaced hot spots in a larger diameter beam will compete for energy from the same background reservoir as if each of them is an independent beam. The consequence of this competition would be such that the hot spots do not have enough energy to develop fully into maturity and result in weak, unstable filaments. From the point of view of R-FIBS, this situation needs to be avoided. In the opposite, the hot spots located inside a small diameter beam are close to each other. Their competition will be most likely in a constructive way due to the light field interference among them. It gives rise to strong and consistent filaments [49,50]. Since in our experimental scheme filamentation starts near the geometrical focus and the beam size is already small at this position, the competition of multiple filaments will take place in a constructive way. As a result, consistent and strong R-FIBS signal shall be guaranteed. This is what we have observed in Figs. 2 and 3.

### 4. Summary

In conclusion, we have demonstrated that the usage of a simple telescope as sending optics could greatly improve the performance of remote filament-induced breakdown spectroscopy. The operational purpose of the telescope is to produce strong and short filaments at a distance as long as a few tens of meters. Because the filaments are short, white light continuum inside R-FIBS spectrum is negligible, realizing non-gated R-FIBS. And because the filaments are strong, the resulting line emission is impressively intense. The extrapolated detection limit of the aluminum sample reaches a few kilometers in distance and some ppm in terms of minor element concentration when the sample is located 50 m away from the detection system. We believe that our result will help to push R-FIBS towards a more versatile and powerful diagnosis tool.

### Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Reference line (nm)</th>
<th>Signal intensity (ICCD counts)</th>
<th>Concentration (% w/w)</th>
<th>Detection limit (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>279.55</td>
<td>38,818.4</td>
<td>0.8</td>
<td>0.0033</td>
</tr>
<tr>
<td>Cu</td>
<td>324.75</td>
<td>6380.0</td>
<td>0.15</td>
<td>0.0038</td>
</tr>
<tr>
<td>Si</td>
<td>288.16</td>
<td>2808.3</td>
<td>0.4</td>
<td>0.022</td>
</tr>
<tr>
<td>Cr</td>
<td>357.87</td>
<td>8016.7</td>
<td>0.04–0.35</td>
<td>0.0008–0.0069</td>
</tr>
</tbody>
</table>

Fig. 3. Signal intensity extrapolation of (a) Al I: 396.15 nm line as function of distance; (b) Mg II: 279.55 nm lines as function of concentration. σ: standard deviation of ICCD background. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
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References


