Long-distance remote laser-induced breakdown spectroscopy using filamentation in air

Kamil Stelmaszczyk and Philipp Rohwetter
Teramobile, Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

Guillaume Méjean, Jin Yu, Estelle Salmon, Jérôme Kasparian,[a)]
Roland Ackermann, and Jean-Pierre Wolf
Teramobile, LASIM, UMR CNRS 5579, Université Claude Bernard Lyon 1, 43 bd du 11 Novembre 1918, F-69622 Villeurbanne Cedex, France

Ludger Wöste
Teramobile, Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

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We demonstrate remote elemental analysis at distances up to 90 m, using a laser-induced breakdown spectroscopy scheme based on filamentation induced by the nonlinear propagation of unfocused ultrashort laser pulses. A detailed signal analysis suggests that this technique, remote filament-induced breakdown spectroscopy, can be extended up to the kilometer range. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1812843]

Laser-induced breakdown spectroscopy (LIBS)[1] provides a versatile analytical tool for real-time surface analysis of metals,[2] plastics,[3,4] minerals,[5,6] aerosols, biological tissues[7] or liquids. LIBS relies on local plasma generation using a strongly focused laser beam, generally a *Q*-switched Nd:yttrium–aluminum–garnet laser. The emission spectrum of the plasma is used for fast and quantitative elemental analysis, with typical detection limits in the range of several to several hundreds of ppm for most elements. To improve the ablation rates in LIBS measurements, subpicosecond laser pulses have been recently used,[2,8–10] with a strong improvement of the measurement reproducibility. The use of a broadband detection system makes the technique versatile, since there is no need for *a priori* knowledge of the species to be detected. The versatility and ease of use of LIBS led to practical applications such as the control of industrial processes,[11] environmental monitoring,[12] waste management,[3,4] medical diagnostics,[7] or space research.[5,6]

Moreover, supported by the development of compact and reliable spectrometers as well as diode-pumped solid-state lasers, portable LIBS systems[6,13] emerged for *in situ* field applications such as the analysis of old painting for archaeology[14] or food analysis. However, applications in hostile environments, for example, the identification of highly radioactive nuclear waste[15] or the monitoring of molten alloys,[16] require remote analysis. LIBS is particularly suitable for such purposes, since the samples need no preparation and must only be directly visible from the operation site. A remote-sensing LIBS technique, based on long-range focusing and remote light collection, has recently been demonstrated to reach distances up to 80 m.[17] But diffraction limits the delivery of high laser intensity (at least 10^{12} W/cm^2 in the femtosecond regime[2]) at further distances using linear optics, which would require even longer focal lengths and prohibitively large optics. Moreover, atmospheric turbulence may reduce the intensity at the focus.

In this letter, we show that the self-guided filaments generated by high-power, ultrashort laser pulses[18–23] can overcome the diffraction limit and deliver high laser intensities at remote locations without focusing, allowing a remote filament-induced breakdown spectroscopy (R-FIBS) scheme. Filaments arise in nonlinear propagation of ultrashort laser pulses, due to the balance between Kerr self-focusing and defocusing caused by the tiny plasma generated in the air. They carry intensities in the range of 10^{13} W/cm^2 (Ref. 19) over several kilometers.[24,25] Such intensity is above the threshold for laser ablation on metal samples using femtosecond pulses.[26,27] We demonstrate R-FIBS measurements at distances up to 90 m, limited in our experiment by the available free space in front of the laser. Our data suggest, however, that R-FIBS can be successfully applied up to the kilometer range.

The experimental setup is depicted in Fig. 1. The *Teramobile*[28] laser source provided 250 mJ pulses centered at 800 nm, at the repetition rate of 10 Hz. The beam was

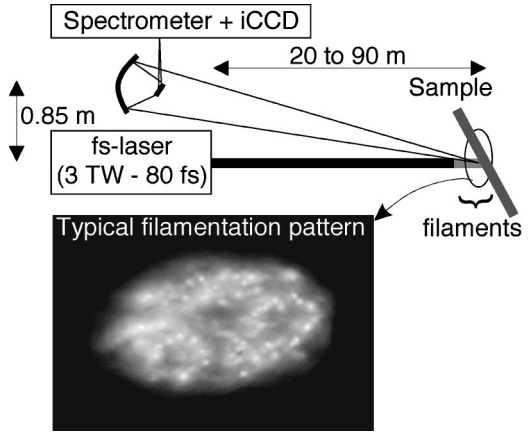

FIG. 1. Experimental setup. Right: beam profile near to the sample showing multifilamentation with typically 30 filaments across the beam.

[a)]Author to whom correspondence should be addressed; electronic mail: jkaspari@lasim.univ-lyon1.fr

emitted collimated, with a diameter of 3 cm. It hit the sample after propagating 20–90 m. The minimum pulse duration at the exit of the compressor was 80 fs. However, to set the position of the filament onset several meters (typically 7–8 m) before the sample, the pulses were shaped with a tunable negative chirp,[23,28] corresponding to pulse durations up to 800 fs. A typical multiple-filamentation pattern, exhibiting around 30 filaments across the beam profile, was observed on the sample (see Fig. 1). The optimal chirp also corresponded to the most intense acoustic shockwave, i.e., to the most intense ablation on the material. The shot to shot excursion of the filament across the large beam cross section spread the damage region on the material over a surface of several cm^2. Therefore, the ablated depth was negligible, even after as many as several 10^5 shots. This allows for noninvasive analysis. Two samples were investigated: raw, industrial-grade copper and steel plates without any surface preparation.

The backward-emitted signal was collected with a 20 cm telescope and analyzed with a time-gated optical multichannel analyzer (Chromex IS-SM 500 imaging spectrometer and Princeton PI Max 1024 HQ ICCD camera), located near the laser. An adequate time gating of the detector eliminated the white-light continuum generated in the filaments by self-phase modulation in air, and reflected elastically on the sample. Contrary to the results of Angel *et al.* with a focused femtosecond beam,[2] we observed no broadband blackbody emission on the 100 ns time scale, showing that the filament-excited plasma is cold, providing a better contrast than in classical LIBS. The FIBS emission was found to be anisotropic with respect to the tilt angle of the sample. However, in order to demonstrate the capability of the R-FIBS also under adverse conditions, we used tilt angles away from the maximum for our measurements.

Figure 2 presents the emission spectra obtained from copper and steel samples located 90 m away from the laser and detection systems. The typical lines of Cu *I* and Fe *I* in the 520 nm region are clearly visible, showing that R-FIBS can perform remote elemental analysis at a distance of 90 m. Although these spectra have been integrated over 10 000 shots, unambiguous spectra could be obtained with only 1000 shots, i.e., less than 2 min at 10 Hz, allowing almost real-time monitoring. Under the same conditions, uncompressed (200 ps) and unseeded (typically 5 ns) laser pulses yield neither ablation nor LIBS signal. Moreover, signal with the femtosecond beam was only observed when the chirp was adjusted so that filaments actually hit the sample. This proves that the observed signal has been generated by the filaments, defining a LIBS scheme for remote analysis.

The measured R-FIBS signal did not depend on the sample distance R, besides the $1/R^2$ geometrical term due to the solid angle collected by the telescope (Fig. 3). However, due to the $1/R^2$ term, the signal-to-noise ratio decreases with the detection distance, and its extrapolated value drops to 1 around 150 m (see dash-dotted line in Fig. 3). This distance must be seen as a lower limit, since the poor coupling into our detection system could be improved, with an expected signal enhancement by a factor of 100, hence allowing R-FIBS measurements at distances up to the kilometer range, comparable with the filament propagation distance.[25] This range opens the way for applications in hostile environments.

We further checked that no intrinsic signal loss occurs, by performing a local measurement, hence without the geometrical term. In that purpose, we kept a fixed, short distance (7 m) between the detection system and the sample, and we moved the laser away. As expected, the measured signal did not depend significantly on the propagation distance of the laser pulses before the filaments hit the sample, at least up to 90 m of propagation. Such behavior is in strong contrast with remote-LIBS excited by a focused beam.[8,16] Here, the incident fluence on the sample decreases with focusing distance since diffraction leads to a beam waist proportional to the measurement distance. Hence, the ionization efficiency falls down when the distance is increased. Since the plasma generation is a multiphoton process, this decrease is not fully balanced by the increase in the illuminated surface on the sample. The simulation of such distance dependence, in the case of the three-photon ionization of Cu at 800 nm,[29] is displayed for comparison in Fig. 3 (solid curve).

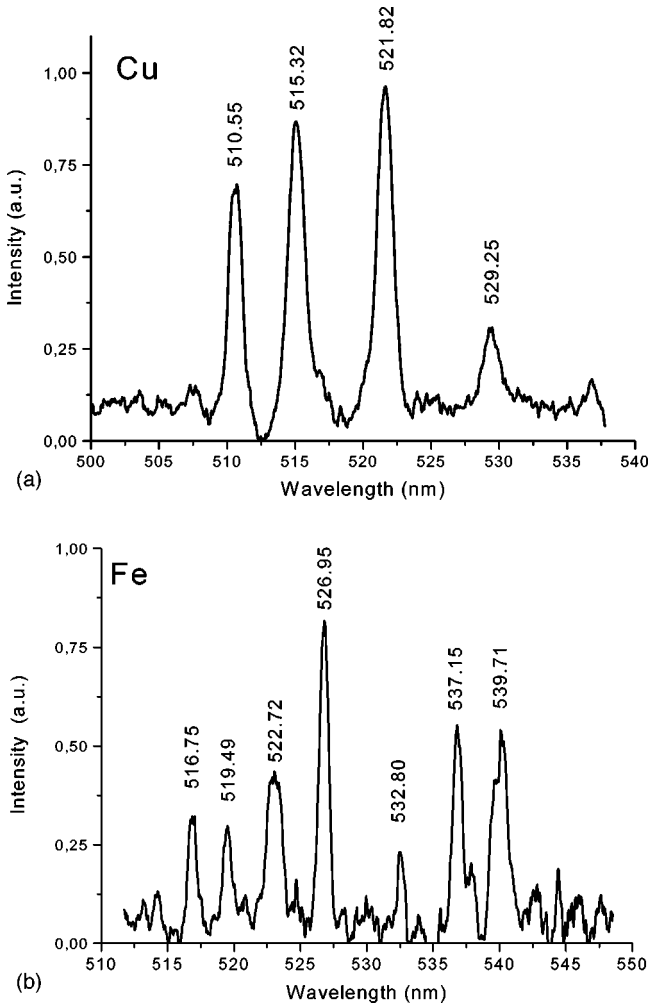

FIG. 2. R-FIBS spectra of copper (a) and steel (b), measured at 90 m distance.

As a conclusion, we have demonstrated a noninvasive, remote optical analysis technique, R-FIBS, up to 90 m, with possible extension up to the kilometer range. This technique is based on filamentation induced by the nonlinear propagation of ultrashort laser pulses. The filaments are able to overcome linear focusing limits of longer pulses, and deliver extremely high laser intensities (10^{13} W/cm^2) at remote distances. This technique, which only requires reasonable laser energies, can be practical for versatile remote analysis on hazardous or unreachable spots, such as polluted sites, nuclear plants or chemical leakages.[30]

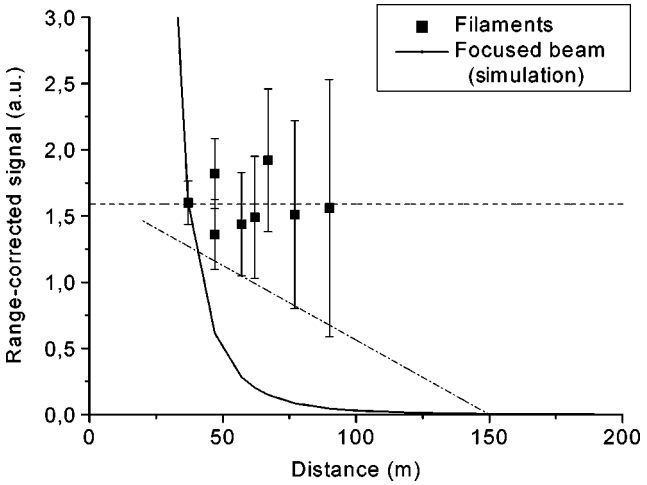

FIG. 3. Distance dependence of the range-corrected R-FIBS signal from the 521.8 nm line of copper.

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[30]Since this letter was accepted, we have detected the 395 plasma line from an aluminium sample located 180 m away from the laser source. This demonstrates further the capability of R-FIBS to perform experiments at long distances.