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HIGHLIGHTS

Laser-induced breakdown spectroscopy in extreme environments

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Laser-induced breakdown spectroscopy (LIBS) is basically an atomic emission spectroscopy of laser plasma [1]. In principle, LIBS can be used in any environments that are transparent to the irradiation laser and to the emitting light from the breakdown plasma. Therefore, solid surfaces not only in gaseous or vacuum environment but also in liquid environment can be a target. Among the various laboratory-based elemental analysis techniques, such as XRF [2], ICP-MS [3], ICP-AES, and others [4], LIBS is unique in that it does not require sample pretreatment. This enables us to use LIBS as an on-site elemental analysis technique. Generally, the sensitivity of LIBS is relatively low compared with mass spectroscopy-based methods or radiometric analysis. Efforts have been made to improve its sensitivity by sample pretreatment; for example, metal nanoparticle deposition onto the target surface to enhance the signal (nanoparticle-enhanced LIBS) [5, 6]. However, such methods cannot take advantage of LIBS' ability to measure samples in situ without sample pretreatment. Despite the drawback of relatively low sensitivity, the advantage of no sample pretreatment allows wide variety of applications in various fields, not only laboratory analysis of the samples unfeasible for pretreatment such as elemental mapping of biological samples, but also on-site analysis in industrial processes. For example, coal analysis for quality control, waste sorting for recycling, analysis of the carbon content in steel production lines, analysis of nuclear waste for decommission, and so on [7]. Among various applications, the capability of on-site analysis seems to be most effective in the applications to in situ analyses in extreme environments, namely deep-sea and planetary explorations.

The use of LIBS in space exploration was first demonstrated by NASA's Mars Science Laboratory mission in 2011. The space LIBS system ChemCam [8, 9] was carried by a Mars rover Curiosity. ChemCam is designed for the Mars environment, namely rarefied CO_2 gas environment less than ~ 1 kPa [10], and for the remote operation. It has an ability to focus laser remotely up to 7 m. The overview of the mission and scientific contributions are summarized in the review article of Vasavada [11]. More recently, in 2020, NASA has launched a new Mars Rover Perseverance equipped with SuperCam, which is a suite of five techniques including LIBS. Details are given in a review article by Maurice et al.[12].

Application of on-site LIBS was extended to deep sea in the last decade. As mentioned above, laser plasma can be produced even in water, so that in situ analysis of solid material in water (underwater LIBS) is in principle possible [13]. However, the plasma confined in water emits continuous spectra, just like the emission from heated solids. The double pulse irradiation mitigates this effect and enables us to obtain atomic spectral lines even in water. Laserna, et al. have developed a fiber-optic LIBS with gas purge system and applied to a solid sample in the 30-m-depth sea water [14]. The same group developed a double pulse stand-off LIBS to apply to deeper sea [15]. Sakka et al. have shown that the irradiation of a long-duration single pulse of ~ 150 ns gives well-defined narrow spectral lines in water [16]. Thornton et al. have shown that the well-defined lines can be obtained with the long pulse even in the hydrostatic pressure of 3000 m in depth [17] and developed a 3000-m-rated LIBS instrument using a long pulse laser [18]. Clear spectral lines feasible for quantitative analysis were observed even for natural rocks around hydrothermal vent in the depth of 1000 m [18]. In general, LIBS has relatively large pulse-to-pulse instability, which results in an inaccuracy in quantitative analysis. This is rather serious in underwater LIBS. To improve the accuracy of quantitative analysis, Takahashi et al. applied calibration-free method [19], partial least squares (PLS) regression analysis [20], and artificial neural network (ANN) [21] to improve analytical performance of underwater LIBS spectra. More details are reviewed in the literature [22].

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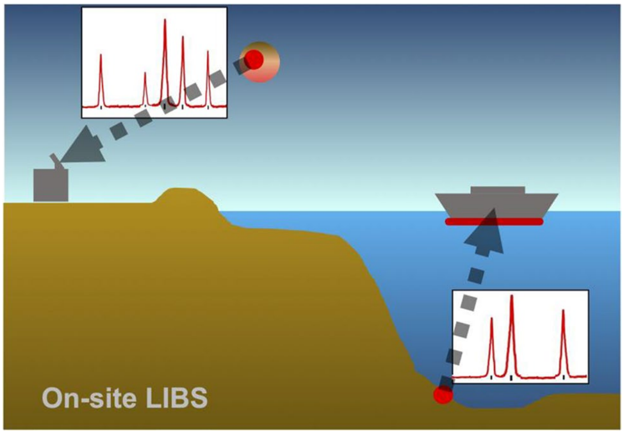

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