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Investigation of helium addition for laser-induced plasma spectroscopy of pure gas phase systems: Analyte interactions and signal enhancement ☆

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Abstract

The role of helium addition on the analyte signal enhancement in laser-induced breakdown spectroscopy for analysis of pure gaseous systems was examined using carbon and hydrogen atomic emission lines. Increased analyte response, as measured by peak-to-base and signal-to-noise ratios, was observed with increasing helium addition, with maximum enhancement approaching a factor of 7. Additional measurements revealed a significant decrease in plasma electron density with increasing helium addition. To explore the mechanisms of analyte signal enhancement, the helium emission lines were also examined and found to be effectively quenched with nitrogen addition. In consideration of the data, it is concluded that the role of metastable helium is not as important as the overall changes in plasma properties, namely electron density and laser-plasma coupling. Helium addition is concluded to affect the electron density via Penning ionization, as well as to play a role in the initial plasma breakdown processes.

Keywords: LIBS; Laser-induced plasma; Metastable

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) has been widely explored for the analysis of solids, while less attention has been focused on the analysis of liquids, gases and aerosol samples. Nonetheless, some of the pioneering LIBS work was focused on aerosol analysis [1,2], and much of the early experimental and theoretical studies examined the laser-induced breakdown of gases [3]. In recent studies, LIBS has been applied to sample and analyze aerosol populations, including ambient air, using various implementations including single-shot analysis to take advantage of the discrete plasma volume [4–10]. However, gains in signal-to-noise ratios typically realized with ensemble averaging are not applicable with single-shot analysis, therefore it is important to maximize the signal and precision on a shot-to-shot basis [11,12]. For analysis of trace elements contained within aerosol particles (e.g. analysis of single, aerosolized spores), the analyte mass of targeted elements may extend to the single fg level, which may be near or below the detection limits for single-shot LIBS [7]. Accordingly, to further establish single-shot LIBS-based techniques as an integrated analytical tool for detection and quantitative analysis of aerosols and dilute gaseous species, it is desirable to seek improvements in the precision and the overall method detection limit. In earlier studies, we have explored these goals in terms of the laser-plasma coupling [11], the laser pulse stability [13], and the use of double-pulse laser excitation [14]. In the current work, the effects of helium addition to the gaseous analyte sample stream are explored as a means to further improve the LIBS signal response.

The examination of helium use with laser-induced plasmas is not a new concept, with studies going back over two decades. Kuzuya et al. reported that emission line-to-continuum ratios were maximized in a reduced-pressure helium atmosphere for the analysis of several solid metals [15]. Time-resolved emission characteristics were explored for solid aluminum and copper targets, as well as with gas breakdown, for plasmas in helium [16]. They examined the roles of helium in energy transfer and

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corresponding signal enhancement, concluding that metastable helium can act as a significant energy reservoir, providing energy for ionization and excitation of excited states. Brust et al. performed detailed measurements of the collision cross-sections for Mg and Ca ions in a helium buffer gas during the laser ablation of solid samples, including comparisons with theoretical treatment [17]. Lee et al. also explored the roles of helium as a cover gas for laser-induced plasma analysis of copper targets, discussing the relative effects of ionization potential and diffusion coefficients on the resulting analyte signal [18]. More recently, Tran et al. used LIBS for analysis of halogens in organic solids for various buffer gases [19]. Helium was found to produce the optimal signal-to-noise ratio in comparison to air and argon, and resulted in reduced line broadening. Contemporary studies by Kurniawan and co-workers have specifically addressed the role of helium for enhancement of hydrogen analysis in solid samples, including zircaloy-4 alloys, via the LIBS technique [20–24]. In their studies, hydrogen emission intensities were enhanced while Stark broadening was reduced through the use of helium breakdown, using both single and double-laser LIBS methodologies. They attribute their findings to direct excitation of hydrogen emission from metastable excited state helium atoms.

In related studies other than laser-induced plasmas, Wagatsuma and Hirokawa have studied the effects of helium addition in a glow discharge reactor by analysis of the Ar II emission lines [25]. They found that when the excitation energy of the Ar II lines was less than the internal energy of the helium metastable states, the intensity of the Ar II lines were significantly increased, while in contrast, they found a reduction in emission intensity when the excitation energy exceeded the He metastable state. Helium has also been used and studied in microwave-induced plasmas [26–31]. As an example, Clay and Niemczyk have studied the effects of metastable energy transfer for metastable nitrogen, and reported that at nitrogen concentrations above 3%, the influence of metastable nitrogen is quite significant [26]. In a more recent paper, Naveed et al. examined the effects of helium gas mixing on production of active species in nitrogen plasmas [31]. They specifically discuss the role of metastable helium in energy transfer to molecular nitrogen via the Penning effect in the context of the relative energy states.

While the above studies are by no means intended to be a comprehensive review of the relevant literature, in concert, they do suggest the careful investigation of helium addition for analysis of purely gas phase analyte systems, pursuant to the analysis of aerosol systems. Regarding aerosol analysis in particular, one must be careful to consider the decoupling of changes in bulk plasma properties as compared to effects limited to regions about individual particles. For example, the robustness of the gas-phase laser-induced breakdown process is often attributed to studies by Yalcin and co-workers, in which the overall plasma temperature and electron density were found to be remarkably independent of gas composition, including comparable plasma conditions for nitrogen, helium with 15% nitrogen, sulfur hexafluoride with 14% nitrogen, humidified nitrogen, and a nitrogen magnesium aerosol [32,33]. However, recent measurements of single aerosol particles in laser-induced plasmas reveal that plasma–particle interactions are confined to relatively small regions within the larger plasma volume [34], hence the potential to impact analyte signals independent of the overall plasma parameters is intriguing. With these comments in mind, the current study is focused on detailed analysis of the effect of helium addition on the analytical figures of merit and related plasma properties for analysis of purely gas-phase systems.

2. Experimental methods

A Q-switched Nd:YAG (Continuum Precision II) laser operating at its fundamental wavelength of 1064 nm and at a repetition rate of 5 Hz was used for all experiments. A schematic of the optical configuration is shown in Fig. 1. A laser beam energy of 320 mJ/pulse (pulse-to-pulse stability less than 0.5% RSD) was used for all experiments. The laser beam was focused to the center of the sample chamber (a five-way vacuum cross) using a UV-grade plano-convex lens with 100-mm focal length. The laser pulse energy was sufficient to create a laser-induced breakdown for every laser pulse over all gas compositions explored.

Spectral emission from the laser-induced plasma was collected via backscatter using a pierced mirror and focused onto a fiber optic bundle, as shown in Fig. 1, and subsequently coupled to the spectrometer. The light was then dispersed by the 0.275-m spectrometer (Acton SpectraPro-275) and finally recorded by a 256×1024 element intensified CCD array. The spectrometer used a 2400 groove/mm grating, which provided an

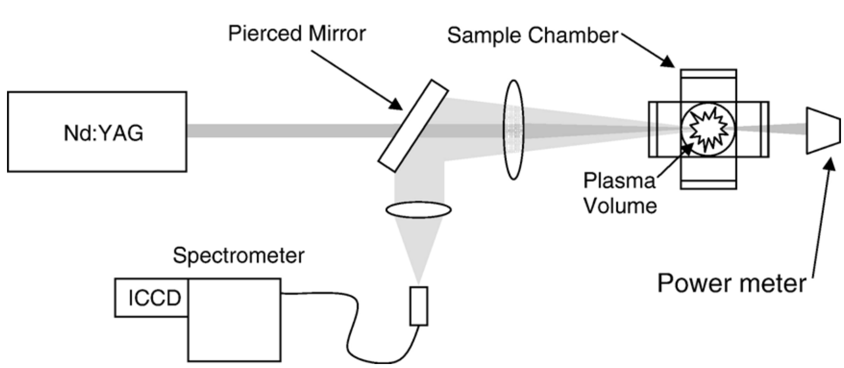

Fig. 1. Experimental set-up for LIBS measurements, showing the power meter in place for transmission measurements.