Laser Ablation – Laser Induced Fluorescence (LA-LIF) for Arsenic Detection Under Argon

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Abstract

Laser Ablation-Laser Induced Fluorescence (LA-LIF) employs laser-induced fluorescence (LIF) in a transient laser ablation plasma for elemental measurements. Laser-induced fluorescence is incredibly rapid, requiring no sample preparation and may be applicable to measurements of arsenic in rice bran using a broadband ArF laser to excite the arsenic via its 193.76 nm absorption transition. This study investigates the experimental parameters affecting the viability of detection in argon plasma atmospheres compared to helium. Plasmas under argon required larger inter-laser delays to compensate for high electron number densities and less thermally conductive plasmas to resolve the arsenic transition and generate adequate signal to background ratio (SBR). Argon cover gas demonstrated a lack of saturation at the required late inter-laser delays as expected since previous helium data showed a softer saturation curve at increasingly long time delays. The mechanism for the SBR-limiting background fluorescence appeared to be single nearby transitions of neutral iron atoms. Further experimentation with a narrowband ArF excimer will be required to improve the current arsenic limit of detection (LOD).

Keywords: LA-LIF, Arsenic, LOD

1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is a rapid trace element detection technique employed in a variety of applications.[1-4] In practice, LIBS employs an ablation laser that vaporizes and ionizes a portion of the sample. The hot transient plasma then emits both thermal emission from the excited atoms and continuum blackbody radiation from the accelerating and recombining free electrons. Laser Ablation Laser Induced Fluorescence (LA-LIF or laser ablation laser-excited atomic fluorescence, LA-LEAF) sacrifices the simplicity of LIBS with an additional resonant laser to improve the LOD. This additional laser lowers the LIBS limit of detection by approximately two orders of magnitude by decoupling analyte emission from the electron continuum and thermal line emission of matrix species.[5] LA-LIF allows a transient LIBS plasma to cool and recombine, and then intercepts the cooled vapor with an excitation laser to induce athermal fluorescence.[6] This excitation process uses an approximately monochromatic excitation laser to selectively induce analyte fluorescence via a single atomic transition, improving selectivity. Plume Laser Induced Fluorescence (PLIF), suggested by Wang et al., provides a nonselective signal enhancement in a LIBS plasma with a deep UV laser pulse.[7] In contrast to LA-LIF, PLIF's multianalyte detection relies on the broadening of the atomic energy states arising from the high atom number densities and is non-selective, though it does show reduced continuum background.

Although this research primarily uses NIST steel samples with relatively uniform and known concentrations of arsenic, it aims to improve the limit of detection to encompass known concentrations of arsenic in rice (0.08-0.2 ppm and 10x higher in the bran).[6,8] It is currently unclear how the arsenic contaminates the rice.[8] While achieving LODs

adequate for measurement in ground rice samples may be unreasonable, LA-LIF might allow a rapid probe of the arsenic levels in the rice bran to serve as a proxy for the whole grain arsenic content. LIBS alone cannot achieve this with a typical LOD on the order of 10 ppm.[6] LA-LIF will improve selectivity and LOD of LIBS using single wavelength excitation. Figure 1 shows the difference between LIBS and LA-LIF emission spectra. The LIBS spectrum has
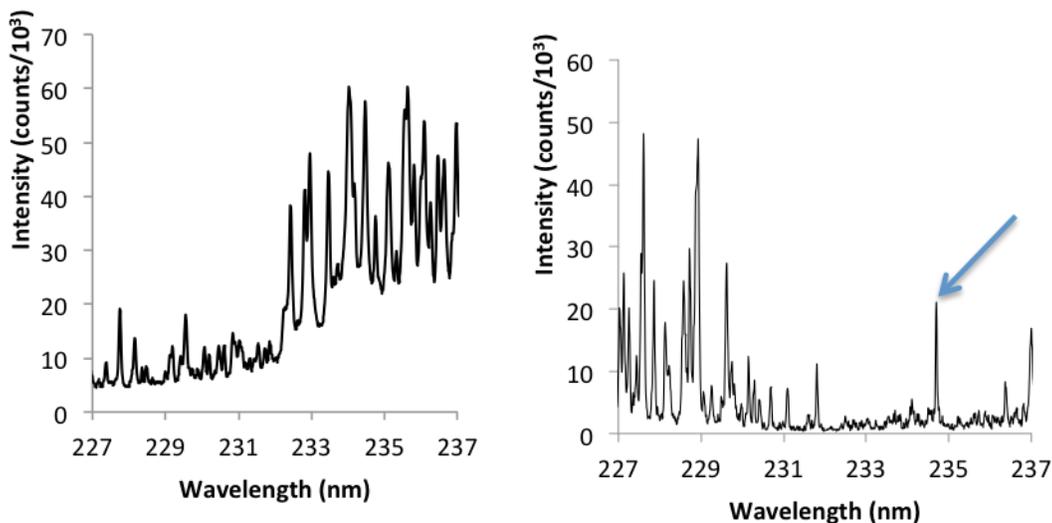

Figure 1. LIBS spectrum of NIST steel sample containing 520 ppm As (left) for comparison with the LA-LIF spectrum of a NIST steel sample containing 35 ppm As (right). The blue arrow indicates the arsenic transition.

a higher baseline background radiation and the arsenic transition near 235 nm is indistinguishable in the high-density cluster of iron transitions. The LA-LIF spectrum has a clear arsenic transition and negligible background continuum, and appears to be a superior technique for single-analyte trace quantitation. This research uses a 193.3 nm argon fluoride excitation pulsed laser (ArF excimer) to re-excited arsenic atoms in steel via arsenic's absorption at 193.76 nm to induce emission at 234.98 nm. This application of LA-LIF significantly improves the LOD of arsenic in steel.

Hueber et al. previously observed and quantified arsenic in inductively coupled plasmas (ICPs) and flames using the same ArF excimer-induced fluorescence scheme proposed in the present study. This group reported a fairly poor limit of detection due to the nonspecific excitation from a standard broadband ArF excimer, resulting in background fluorescence of matrix atoms and molecules.[9] This background fluorescence proves challenging in a steel matrix due to the large number of iron absorption transitions surrounding the arsenic absorption and emission lines. LIF in ICPs and flames requires extensive sample preparation to transfer the arsenic atoms into the dissolved phase and inject them into the ICP. Ablation avoids this requirement, driving our interest in LA-LIF.

Our lab has previously explored LA-LIF arsenic detection primarily under helium cover gas.[6] The helium atmosphere is known to produce cool laser ablation plasmas and lower fluorescence quenching, but is expensive and consumes a non-renewable resource.[10] Argon cover typically produces hotter plasmas and is more prone to fluorescence quenching, but is cheap, abundant, and renewable.[10] This study explores argon as a plasma atmosphere and complements our previous helium study.

2. Experimental

2.1 Dual-Pulse Laser System

NIST steel samples were ablated using a 355 nm, 6 ns Continuum Surelite neodymium yttrium aluminum garnet pulsed laser (Nd:YAG or further abbreviated YAG) triggered at 10 Hz with a DG645 delay generator (Stanford Research Systems). The YAG produced pulse energies between 14 mJ and 18 mJ. The laser pulse was focused on the sample surface with a plano convex lens (f.l. = 15 cm) slightly below the sample surface to prevent cover gas breakdown. A standard broadband GAM EX5a 193.3 nm argon fluoride pulsed laser (ArF excimer) induced

fluorescence of the arsenic via its 193.76 nm absorption transition. The ArF excimer produced a maximum energy of 14 mJ that could be attenuated appropriately using fused silica and fused quartz microscope slides and cuvettes. The optical set up is shown in Figure 2. The time delay between the ablation laser and excitation laser (inter-laser delay) was controlled with a DG645 delay generator. The ICCD was triggered with the "sync out" output of the ArF laser because of the substantial jitter between the ArF trigger pulse and the ArF emission. Samples were rotated after each spectrum to preserve sample surface quality.
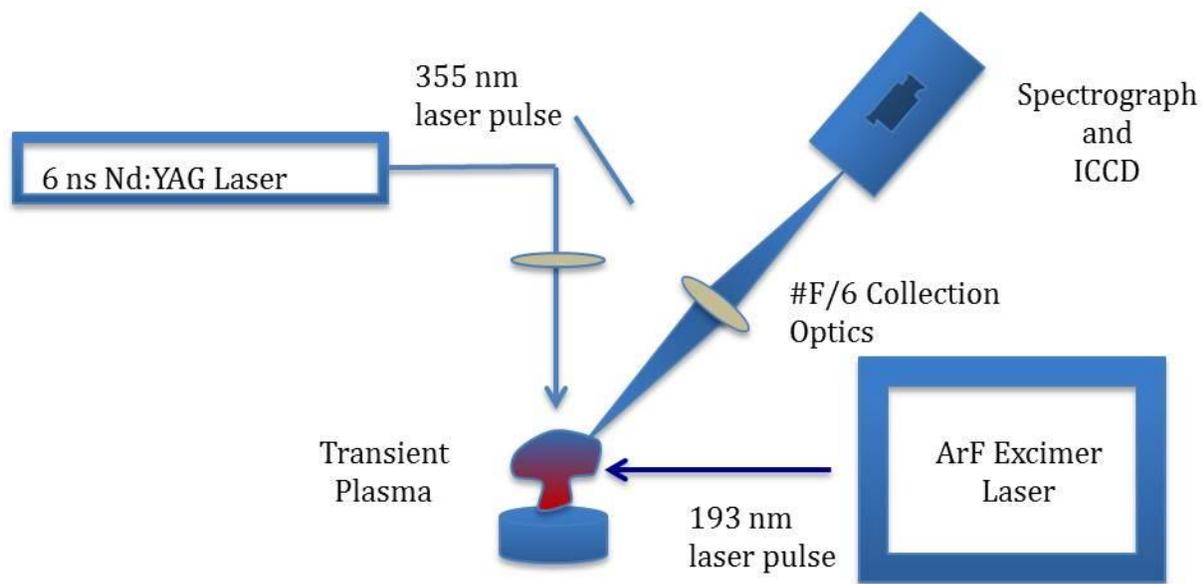

Figure 2. Diagram of optics

2.2 Collection Optics

An Andor Shamrock 0.5 m focal length spectrograph selected the fluorescence. Detection of the arsenic emission line at 234.98 nm was with an ICCD camera (Andor, gen. II intensifier). Ten shots were accumulated on the camera's cooled CCD chip before readout of a spectrum. The ICCD gate, triggered by the sync out signal from the ArF excimer, was 8 ns wide and centered over the 8 ns-wide ArF pulse. The spectra were analyzed using LabView programs written in-house.

2.3 Gas Introduction Setup

Because the plasma atmosphere influences the evolution and observed spectra of a LIBS plasma, the atmosphere was controlled by blowing cover gas onto the sample through a tapered tube positioned approximately 1 centimeter above the sample surface. The ablation laser pulse propagated through the nozzle, with optical access provided by a fused silica window opposite the nozzle's exit aperture. The gas system is omitted in Figure 2 for clarity.

3. Results and Discussion

3.1 Effects Of Inter-Laser Delay

The inter-laser time delay affects the LOD of LA-LIF, with the optimum delay depending on the physical properties of the cover gas. Helium requires a relatively short inter-laser delay, around 18μs, to optimize signal to background ratio due to the gas' high thermal conductivity and high ionization energy.[11] Figure 3, on the other hand, displays spectra under argon cover gas after inter-laser delays of 30μs and 20μs. The arsenic transition was not well resolved

for the delays used in helium measurements (e.g. ~20 μs). The transition did eventually become apparent after the significantly larger inter-laser delay. Presumably, the plasmas under argon required a substantially longer time delay to compensate for argon's lower thermal conductivity and subsequently slower cooling and recombination.
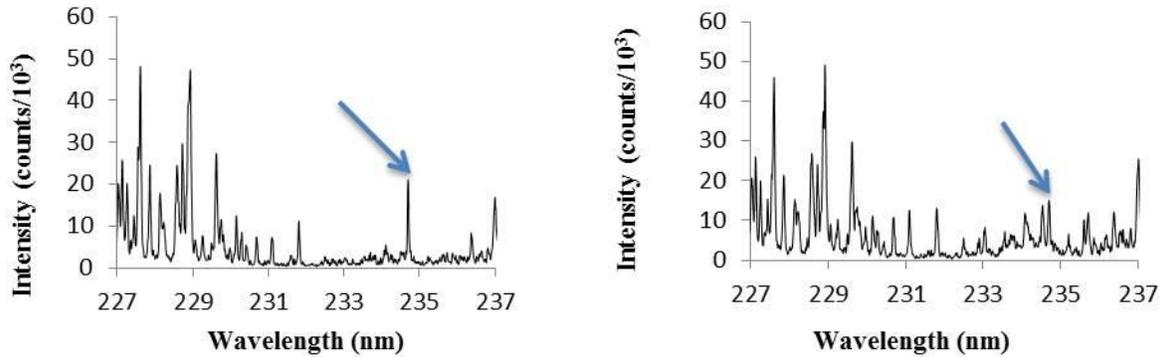

Figure 3. LA-LIF spectra taken under argon with 35ppm [As] NIST steel samples. The inter-laser delay for the spectra, left and right, were 30 μs and 20 μs respectively. The blue arrows indicate the arsenic transition.

3.2 Effects Of Arf Excimer Beam Position

Given that both the ArF laser beam and the LIBS plasmas are small (~ 1 mm), achieving spatial overlap is nontrivial. The arsenic signal was optimized by scanning the ArF beam across the plasma at an inter-laser delay of 30 μs and a height of 2.75 mm above the sample surface. Figure 4 shows the integrated arsenic peak area as a function of the lateral position of the ArF excimer. The results show that the plasma is no wider than 0.4 mm full width at half maximum. The slight deviation from symmetry was likely produced by a misalignment in the crystals responsible for YAG harmonic generation, with some resulting asymmetry in the LIBS plume.
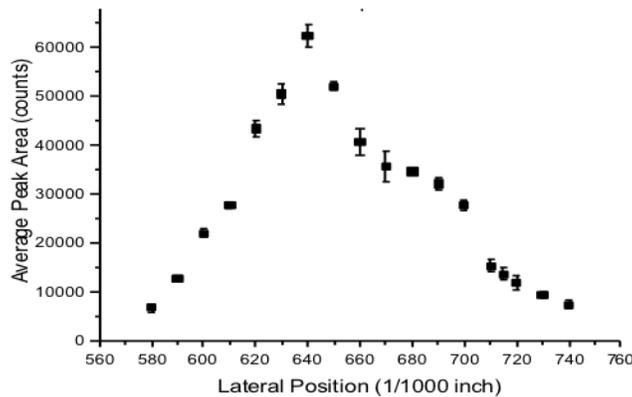

Figure 4. Arsenic signals as a function of ArF beam position over a 35ppm [As] NIST steel sample under argon cover gas. Error bars are the standard error of four time-independent spectra.

Because the LIBS plasma is known to propagate away from the sample surface in the course of its evolution, spectra were taken as a function of height above the surface. In order to optimize the LOD, the signal to background ratio (SBR) was used as a stand in for signal to noise ratio. The iron transition at 234.8 nm was selected as "background" for simplicity. The SBR was studied both as a function of inter-laser delay and excitation beam position above the sample since the plasma is expected to propagate away from the surface over time. Figure 5 investigates the signal to background ratio (SBR) as a function of the vertical positioning of the excitation laser and the inter-laser delay.
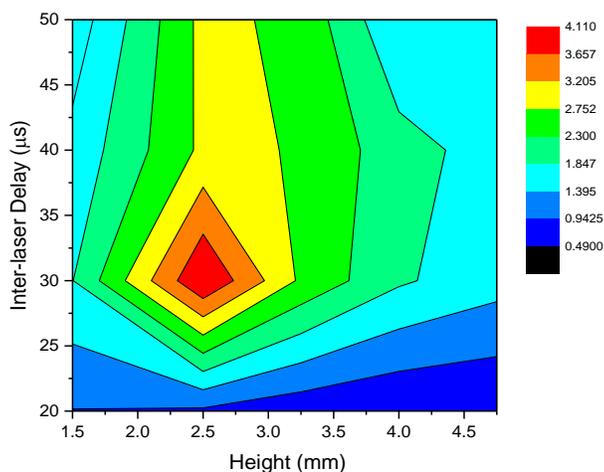
Figure 5. Signal to background ratio under argon as a function of the inter-laser delay and the relative height of the excitation laser. The NIST steel sample contained 35ppm As.

The optimal signal to background ratio occurred at a height of 2.75 mm and an inter-laser delay of 30 µs. The signal to background dropped at inter-laser delays less than 30 µs; the poor SBR at the early delays likely resulted from the thermal emission from the hot argon-buffered plasma. Once the background thermal emission died off, the high SBR region outlined in red falls off slowly beyond 30µs as the plasma dissipates. This is in contrast to the SBR maximum under helium, which peaks at a 18 µs inter-laser delay.[6]

3.3 Effects Of Excitation Laser Energy

Hueber et al. observed saturation of the arsenic LIF signal in ICP plasmas, but not flames, in their CW-reservoir studies.[9] Our lab previously reported a non-standard saturation behavior in arsenic LA-LIF under helium.[6] Saturation studies under argon (Figure 6) demonstrate a similar behavior to that under helium (Figure 7).[6] In general, increasing the inter-laser delay resulted in a softening of the onset of saturation in the helium data. The lack of obvious saturation behavior in the argon data may be a continuation of this trend to the extreme delays necessary for the hotter argon plasma. The mechanism of the shift in the onset of saturation and the softening of the degree of saturation in Figure 7 remains under investigation.
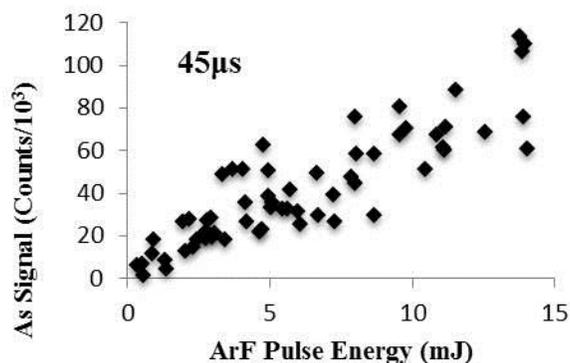

Figure 6. The arsenic signal intensity as a function of ArF laser pulse energy under argon cover gas with an inter-laser delay of 45 µs. The NIST steel sample contained 35 ppm As.

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Figure 7. Arsenic signal intensity as a function of ArF laser pulse energy under helium cover gas. NIST steel sample contained 35ppm As. This figure is reproduced from Reference 6 with permission.

3.4 Mechanism Of Background Fluorescence

Complex matrix materials require rigorous selectivity to re-excite the analyte without generating background in LA-LIF. Iron is a particularly difficult matrix, with a high density of background lines at most wavelengths. While fluorescence spectroscopy should be more selective than emission spectroscopy, the LA-LIF spectra using ArF excitation showed substantial background iron fluorescence. In addition to the possibility of a PLIF-type mechanism, there was potential for a standard one element-one wavelength (selective) origin for the iron fluorescence; the broadband ArF emission spectrum (Figure 8) overlaps a number of ground state and near-ground state lines.[6] Table 1 summarizes candidate iron absorption lines in the vicinity of the ArF spectrum and stokes-shifted iron emission lines that might occur in the vicinity of the 234.98 nm arsenic emission line along with the arsenic lines used in this study.
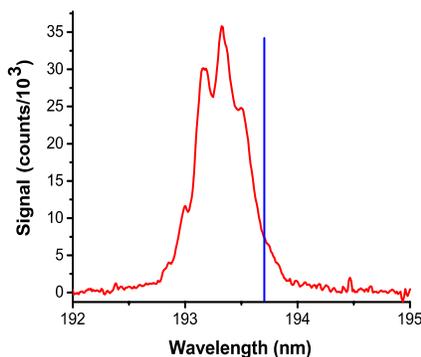

Figure 8. Emission spectrum of a standard broadband GAM EX5a 193.3 nm argon fluoride laser (red trace). The relative location of the arsenic absorption is indicated in blue.

Table 1. Possible iron transition wavelengths and associated Einstein coefficients compared to the desired arsenic transition.[12]

Matrix Species	λ (nm)	E lower (cm^{-1})	E upper (cm^{-1})	A (s^{-1})
Fe II	193.677	668	52300	2.00E+08
Fe II	234.349	0	42658	1.73E+08
Fe II	234.396	2430	45080	3.13E+07
Fe II	234.811	1873	44446	6.50E+07
Fe II	234.830	668	43239	1.15E+08
Fe I	193.454	0	51692	2.50E+07
Fe I	193.727	0	51619	2.20E+07
Fe I	194.066	416	51944	2.60E+07
Fe I	235.041	0	42532	1.60E+05
As I	193.759			2.00E+08
As I	234.980			3.10E+08

While the ionic transitions have the highest transition probabilities, the plasma should not contain a high density of ions at the long delays used in the study. Further research will include a study employing a narrowband ArF excitation laser to sharpen and tune the excimer emission peak and eliminate background fluorescence of nearby individual transitions. Preliminary experiments with the narrowed laser indicate that the iron fluorescence originates in absorption by multiple relatively narrow neutral atomic lines under the ArF gain profile (i.e. not via Wang et al.'s broadband PLIF mechanism).

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4. Conclusions

Although we have previously reported that detection limits under argon and helium are similar (1.6 and 1.0 ppm, respectively), these two gases require very different experimental parameters.[6] Argon demonstrated a similar saturation behavior to long inter-laser delay helium measurements in the excitation energy studies, but required much longer inter-laser delays for adequate signal to background ratio. While ArF-induced LA-LIF is an improvement of the LIBS technique, it does not reach the range of arsenic concentrations in rice. Additionally, we expect detection limits to be worse in organic materials given the possibility of the ArF's exciting molecular fluorescence in the vicinity of the 235 nm emission line. On the other hand, we expect that further experiments with the narrowband ArF excitation laser will continue to improve these results, possibly allowing screening measurements via LA-LIF in rice.

5. Acknowledgements

6. References

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